Physico-Chemical Characterisation Of Surface Defects On Chemically Protective Gloves Used In Agriculture

by

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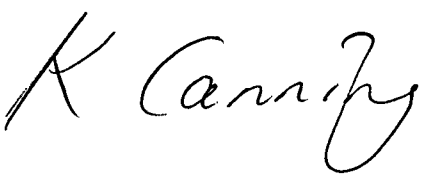

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Abbreviations

ACh	Acetylcholine
AChE	Acetylcholinesterase
Acetyl CoA	Acetyl Coenzyme A
a.i.	Active ingredient
ASTM	American Society for Testing and Materials
BG	Botanical Gardens; code used for gloves from this enterprise (ornamental horticulture)
BT	Breakthrough time
CA	Chromosome aberrations
CAS	Chemical Abstract Number
ChE	Pseudocholinesterase, also known as plasma cholinesterase
CNS	Central nervous system
CPC	Chemical protective clothing
CPG	Chemically protective glove
cps	Counts per second
2,4-D	2,4-dichlorophenoxyacetic acid
DDT	1,1,1-trichloro-2,2,-bis(4-chlorophenyl)ethane
DEDTP	O,O-diethylphosphorodithioate
DEET	N,N-dietyl-m-toluamide
DEP	O,O-diethyl phosphate
DETP	O,O-diethylphosphorothionate
DMDTP	O,O-dimethylphosphorodithioate
DMP	O,O-dimethyl phosphate
DMTP	O,O-dimethyl phosphorothionate
DP	Degree of polymerization (Chapter Three)
DP	Derwent Park; code used for gloves from sheep grazing properties
EC	Emulsifiable concentrate
EDC	Ethylene dichloride
EDS	Energy dispersive X-ray spectrometer
EDTA	Ethylenediaminetetra-acetic acid
EPTC	S-ethyl-N,N,-dipropyl thiocarbamate
ESEM	Environmental scanning electron microscope

ESC	Environmental stress cracking
GC-MS	Gas chromatography-Mass spectrometry
GSED	Gaseous secondary electron detector
Hz	Hertz
IR	Infra red radiation
IUPAC	International Union of Pure And Applied Chemistry
J	Joule: the SI unit for all forms of energy
kV	Kilovolt: see V for volt
L	Lag time
LD_{50}	50% lethal dose
m/z	Mass to charge ratio
NIOSH	National Institute Occupational Safety and Health
NBR	Nitrile-butadiene rubber
NTE	Neuro target esterase
OP	Organophosphorus compound (insecticide)
OPIDN	Organophosphate-induced delayed polyneuropathy
OR	Orcharding areas; code used for gloves from this origin
PPE	Personal protective equipment
PVC	Polyvinyl chloride
S	Poison schedule
SCE	Sister chromatid exchanges
SEM	Scanning electron microscope
SSPR	Steady state permeation rate
SATW	Super atmospheric thin window
T	Torr; a unit of atmospheric pressure commonly used in vacuum technology (1 T = 133 PA)
TEPP	Tetraethyl pyrophosphate
TF	Tahune Fields; code used for gloves from this farming enterprise (mixed horticulture)
Tg	Glass rubber transition
ULV	Ultra Low Volume
UV	Ultraviolet radiation
V	Vegetable; code used for gloves from a vegetable grower
V	Volt: measures the potential accelerating voltage (only pertaining to ESEM methods)
VCM	Vinyl chloride monomer

W	Watt: the SI unit for power
WHO	World Health Organisation
WP	Wettable powders

Chapter One

Introduction

1.1 The Purpose Of The Thesis

Australian agriculture is largely dependent on the use of pesticides. Many pesticides have detrimental effects on human health, and consequently occupational exposure presents a serious problem. Pesticide application can be dangerous work and farmers rely on chemical protective clothing to provide a barrier to dermal exposure. Hands are one of the most often contaminated anatomical sites and therefore gloves are perhaps the most important item of protective apparel.

The principal objective of this thesis is to ascertain the types of chemically protective gloves that are used in agriculture, and to determine if these gloves are suitable for effective protection against chemical exposure to farmers. The hypothesis that evolved from this objective is:

> That, due to poor quality control, no protocols in glove care and patchy promotion of their usage, I predict that chemically protective gloves are inadequate for farmers' needs.

The aims that have evolved from the hypothesis are:

1. to find out what types of protective gloves are being worn by farmers during pesticide application, and to determine the condition, age and maintenance regime of these gloves;
2. to identify and classify the microscopic physical surface defects that occur in new and used gloves and those exposed to simulated field conditions and to compare them statistically;
3. to compare the surface chemical composition of new gloves, used gloves and those subjected to simulated field exposure;
4. to determine if gloves used by farmers are suitable for use in the outdoor environment; and
5. to describe the progress of degradation in gloves exposed to the outdoors to determine their suitability for use outdoors and their life expectancy.

The sampling area was restricted to Tasmania, and although this state is not completely representative of the whole of Australian agriculture, it nevertheless encompasses a wide variety of agricultural production.

1.2 Statistical Approaches

Statistical analyses have been conducted using the program SigmaStat™ (Jandel Scientific Software 1994). A range of statistical tests was used and described with standard statistical abbreviations. Generally the data were not normally distributed and

were often not readily transformed satisfactorily, and therefore non-parametric statistical analyses are dominant. The tests used include; Kruskal-Wallis (H) One Way Analysis of Variance (ANOVA) on Ranks and Mann-Whitney Rank Sum Test (T). The parametric tests used for the normally distributed data include One Way ANOVA and t test (t). Dunn's Test and Student-Newman-Keuls Tests were used when pairwise multiple comparison methods have been necessary following significance. Other abbreviations that occur throughout the text and tables include: P = probability, d.f. = degrees of freedom; and NS = not significant. Each experimental section includes a description of the statistical methods used.

1.3 Defining The Terms

Chemically protective gloves, chemical protective gloves and chemical resistant gloves are synonymous terms and are all used within the literature. Although the first two terms are grammatically incorrect they are more widely used. The first term has been chosen for this thesis as it has previously been used in the Australian context (Bromwich 1992), and is abbreviated to CPGs in this thesis. These gloves are further categorised as supported or unsupported. Supported gloves are lined. Usually a cotton knit hand form is dipped into the polymeric material and allowed to dry on the hand form and therefore the lining is bonded to the polymeric material. Supported gloves are stronger but there is a loss of tactility and dexterity. Unsupported gloves consist only of the polymeric material (Ansell Edmont Industrial undated, p.2).

Throughout the thesis, the term *specimen* refers to the cut out sections of the gloves and the term *sample* refers to the portion of the glove that was punched out of the specimen. It was the samples that were analysed.

The term organophosphorus compounds only refers to insecticides in this thesis and is abbreviated as OPs. These compounds are also known popularly, within the technical literature, as organophosphate insecticides.

Other terms are defined within the thesis and in the list of abbreviations (p.xxiii).

1.4 An Overview Of The Structure Of The Thesis

The thesis is organised according to the following structure. A comprehensive review of the related literature is provided in Chapters Two and Three. Chapters Four to Seven contain the experimental work. The results from the exchange program are detailed first and then throughout the thesis polyvinyl chloride experimental work is discussed prior to nitrile-butadiene rubber.

The focus of Chapter Two is on pesticides, particularly OPs, and occupational exposures. It provides an account of their toxicity and hazards to which farmers are exposed in their working lives. Biological and environmental monitoring studies are evaluated. A review of all these methods has not reached a unanimous finding that hands are the most exposed anatomical site, but, the general trend is towards this region. The degree of exposure is of course related to the task at hand, the pesticide formulation application techniques and prevailing weather. Many of the exposure studies divide their subjects into task oriented situations, which is not applicable to most Tasmanian operators who are usually responsible for the entire process of pesticide application, including mixing and loading. Dermal exposure continues to be the major route inspite of many engineering improvements such as personal protective equipment and mechanical innovations such as adjustable booms. These factors relating to pesticide exposures are discussed in order to demonstrate that farmers can be susceptible to severe health effects through occupational exposure.

Chemically protective gloves provide an important barrier against pesticide exposure in farmers. Chapter Three provides a detailed review of the relevant polymers and CPG literature. Efficacies of CPGs is a subject that has only been of scientific interest since the 1970s, when guides based on degradation processes became available. During the 1980s there was increasing interest in chemical permeation that has continued to the present day. Permeation and penetration of chemicals through gloves are described and provides a background into the status of these gloves. This in turn provides a framework for the original research of this thesis.

Chapter Four provides new information about the types of gloves farmers are wearing when applying pesticides and their macroscopic defects. Personal interviews and questionnaires were undertaken in various rural areas in Tasmania and included agricultural retailers, protective clothing specialists and safety retailers and farmers. An exchange program was instigated where farmers' used gloves were replaced with new gloves. The main types of gloves used by farmers were polyvinyl chloride and nitrile-butadiene rubber, and consequently both were used in the controlled experiments.

Generally the condition of the collected gloves was poor, fewer than half of them being intact. The visible failures included cracks, splits, macropores, punctures and abrasions. It was therefore concluded that farmers need to be encouraged to check their gloves before use. There was no uniformity in the manner the gloves were maintained over their mean life span of two years. Farmers use their CPGs for a variety of pesticide applications, thus demonstrating that most of the single chemical

permeation testing is not ideally applicable to real agricultural situations.

Physical defects on the surface of new and used chemically protective gloves are examined and classified at microscopic level in Chapter Five. This chapter provides new information about the surface defects on CPGs and distinguishes those that result from the manufacturing processes and those that occur with use and exposure to pesticides. The main types of defects identified include cracks, cavities, convexities, slumps and crazing. Contaminants on the surface of these gloves were also investigated.

X-ray microanalysis of the surface of CPGs is described in Chapter Six. The main elements found on these gloves include carbon, oxygen, aluminium, silicon and chlorine. Some of these elements are integral to the glove structure, but there are changes that occur during use and exposure. Phosphorus and sulfur were used as indicators for OP retention. Phosphorus was found to be the more reliable indicator. The interior of polyvinyl chloride gloves was analysed by gas chromatography and mass spectroscopy to determine if pesticide residues were on the interior surfaces of used gloves.

The emphasis of the final experimental chapter is on short and long-term outdoor exposure and OP exposure to CPGs. The short-term exposure studies were of four hours duration and were representative of field conditions where a farmer may use the gloves for a short period and has an OP splashed or spilt on the gloves. The long-term exposure studies took place over seven months. These experiments explore the processes of degradation. Nitrile-butadiene rubber gloves provide superior chemical resistance properties compared to polyvinyl chloride. However, they are not robust enough for outdoor exposure and typical farm work. Previous CPG studies were in controlled laboratory conditions and knowledge about their robustness for real outdoor work did not exist.

Chapter Eight offers a synthesis of the trends revealed from the experimental work and recommendations for future work. This thesis presents a novel approach to the evaluation of CPGs, which is complementary to existing studies. It may well have application to other protective apparel.

Chapter Two

A Synopsis Of Organophosphorus Compounds: History, Health Effects And Exposure Studies

2.1 Introduction

The scientific application of pesticides has been a key element in the remarkable growth of agricultural productivity, since the end of World War 11. However, their use has not been benign and one of the largest occupational risk groups in the world are those people who work with pesticides (Davies 1990). There is an ever expanding awareness of the hazards of pesticides, many of which have insidious human health effects, such as carcinogenesis and delayed nerve diseases (Kurtz *et al.* 1989, p.137).

The term pesticide is a generic term encompassing a wide range of compounds (Moses 1983, p.547). The history of pesticide use is extensive, colourful and becomes incredibly comprehensive and exciting with the advent of modern synthetic chemistry since 1930. Organophosphorus compounds are the most widely used class of insecticides in the world. Classification of these compounds is complex and various systems are used, some of which are based upon chemical structure, toxicity and end use systems. These issues are discussed in the first section of this chapter (2.2–2.3). Exposure to pesticides can be monitored with biological methods and/or environmental methods. Biological monitoring for OP exposure includes analyses of anticholinesterase functions, urinary metabolites and cytogenetic testing. Some of the problems associated with OP poisoning, such as intermediate syndrome and organophosphate-induced delayed polyneuropathy, are briefly described in this section (2.4).

Environmental monitoring involves measuring the pesticide levels within the operator's working environment, which includes their garments and work surfaces. Exposure studies with emphasis on dermal exposure are detailed in this next section (2.5–2.6). The hands are the main anatomical region contaminated during pesticide application. Some of the problems of exposure can be lessened by engineering controls, such as better design of the application equipment, use of personal protective equipment (PPE), which includes all equipment that shields the operator from chemical, physical or thermal hazards (Abbott *et al.* 1987; Forsberg and Mansdorf 1993, pp.96–97) and finally the use of chemical protective clothing (CPC), which includes CPGs (2.7).

2.2 A Short History Of General Pesticide Use

Historically, many resourceful methods have been exploited to control invertebrates, vertebrates and microorganisms in order to maximise the production of food, fibre and forage and to promote public health by vector control. Pesticides used prior to the 1930s were derived from natural resources and involved various techniques over the centuries. Some of the earliest examples date back to classical Grecian and Roman

societies. Homer recorded sulphur fumigation of houses circa 1000 BC (Hassall 1990, p.1). Biblical armies used sulphur and potash to sterilise battlefields (Ware 1989 p.11) and by the sixteenth century arsenicals were being used as insecticides in China. Nicotine, from tobacco extracts, was used to control lace bugs in France during the 1690s and for plum curculio beetles in China (Hassall 1990, p.1; Ebert *et al.* 1988, p.662). Pyrethrum, lime and sulphur combinations were used by 1800–1825 followed by quassia, phosphorus paste and rotenone in 1825–1850. Copper arsenite (Paris green) and kerosene emulsions heralded the scientific application of pesticides and were used as dormant sprays for deciduous fruit trees during the period from 1867–1868 (Ware 1989, pp.10–11). The success of Paris green led to the use of other metals as insecticides, such as lead, zinc and mercury. Organomercury was used as a seed dressing in Germany in 1913 (Hassall 1990, p.2). Calcium arsenate replaced Paris green in the 1920s; at this time there was a great deal of public concern about the use of arsenical pesticides related to toxic residues in treated food products (Ecobichon 1991, p.565).

The genesis of modern synthetic chemistry occurred in the 1930s. By the beginning of World War 11 many pesticides were under experimental investigations. A rapid synthetic chemical expansion of pesticides during the post World War 11 era saw the debut of a plethora of herbicides, insecticides and fungicides (Ecobichon 1991, p. 565). Carbamates were first developed as soil acting herbicides by the British in 1945 and soon afterwards the Swiss developed insecticidal carbamates. Herbicide research in the phenoxyalkanoic group was conducted in Britain and the United States of America (Hassall 1990, p.2). Paul Meuller discovered the insecticidal properties of 1,1,1-trichloro-2,2,-bis(4-chlorophenyl)ethane (DDT) in 1939 and commercial production of DDT and related chlorinated hydrocarbon compounds proliferated from the mid 1940s. These compounds were the major insecticides employed in the 1950s and 1960s. They were cheap, persistent and effective; however public concern over environmental contamination, bioaccumulation and adverse health effects led to strict limitations of their use (Moses 1983, p.547). This encouraged considerable investment in the development OPs as insecticides.

Several exciting pesticide discoveries occurred during the 1950s–1960s. Synthetic pyrethroids, which were far superior to the natural pyrethroids because they were light stable, were developed in Britain and Japan. The triazine herbicides and quaternary ammonium compounds were introduced by Switzerland and Britain respectively. Glyphosate was discovered in the United States of America soon afterwards (Hassall 1990, p.2).

2.2.1 Organophosphorus compounds: an historical perspective

The founder of organic phosphorus chemistry is usually thought to be Lassaigne who reacted ethanol with phosphoric acid to produce triethyl phosphate in 1820. Cleoz discovered thiophosphoric esters in 1847. Michaelis and Becker converted trialkyl phosphites to dialkyl phosphonates in 1897 and in 1903 Michaelis synthesised phosphoramidodichloridates from phosphorus trichloride. During 1854 de Clermont synthesised tetraethyl pyrophosphate by the reaction of the silver salt of pyrophosphoric acid with ethyl iodide, which is known today as TEPP. The insecticidal properties of TEPP were only recognised in 1934 by Gerhard Schrader and it was used as an alternative for nicotine to control aphids (Kurtz *et al.* 1989, p.140). It was not until 1932 that the high toxicity of OPs was recognised by Lane and Kruger who were experimenting with alkylation of the silver salts of monofluorphosphoric acid, a discovery that was consummated by the synthesis of the highly toxic nerve gases tabun and sarin by Schrader in 1937, diisopropyl phosphoro fluoridate (DFP) by Saunders in 1941 and soman by Riser in 1944 (Hassall 1990, p.81).

Schrader is known as the father of OPs because of his research and development of TEPP and synthesis of parathion in 1944 (Chambers 1992, p.4). Following the discovery of parathion there ensued a rapid development and recognition of OPs as powerful and effective insecticides, although all of these early insecticides had high mammalian toxicities. Malathion was an extremely important innovation, presented by American Cyanamid in 1950, because it was the first efficacious insecticide to be efficient and have low mammalian toxicity (Moses 1983, p.547). The increasing resistance problems of the organochlorine compounds permitted the OPs to become the dominant class of insecticides world-wide during the 1970s. The use of chlorinated hydrocarbon insecticides will continue to decline internationally because of their associated environmental hazards (Moretto and Lotti 1993, p.177). Today there are many other classes of insecticides, such as synthetic pyrethroids and carbamates, which compete with OPs in the market place. Nevertheless the OPs remain the most important class of insecticides today (Chambers 1992, p.4).

2.3 Classification Of Organophosphorus Compounds And Other Pesticides

In agriculture there is a wide variety of OPs in use, and although predominantly used as insecticides they also function as fungicides, nematocides, acaricides, herbicides, and plant regulators (Medved and Kagan 1983, p.1637). In this respect their versatility is unsurpassed.

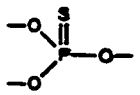
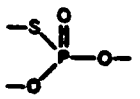
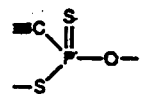
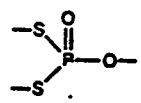
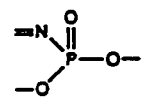
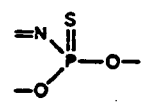
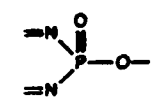
Classification of OPs is complex because they are a very large and diverse family of chemicals. There are at least two hundred organophosphorus esters and from these there are thousands of different formulated products (Ecobichon 1991, p.580). Within this family of chemicals there is an extensive variance between toxicity, and physical, biological and chemical properties (Medved and Kagan 1983, p.1637). In this section chemical classification will be discussed first followed by three other classification systems, which relate to their toxicity, legislative and formulation.

2.3.1 Chemical classification

By definition OP compounds are girdled around a phosphorus atom, and variations within this structure give rise to different classes (Table 2.1). Generalisations are difficult owing to the distinctions within aromatic and aliphatic groups (Racke 1992, p.51). All the insecticides in use have four atoms directly attached to the P atom, three of which are single bonds and the other a double bond. Some OPs are highly reactive, such as the phosphates, and these are useful where short residual activity is desired. The relevant subclasses, partial structures and examples of insecticides are illustrated below (Table 2.1) (Chambers 1992, pp.5–8).

TABLE 2.1

Chemical sub-classes and partial structure of some organophosphorus esters plus insecticide examples

Organophosphorus ester	Partial structure	Examples of insecticides
Phosphates		DDVP Mevinphos
Phosphorothionates		Parathion Diazinon Chlorpyrifos
Phosphorothiolates		Demeton 11 Oxydemetonmethyl Omethoate
Phosphorothionothiolates		Phorate Malathion
Phosphorodithiolates		Ethoprop Ebufos
Phosphoramidates		Fenamiphos Phosfolan
Phosphoramidothionates		Propetamphos Isofenphos
Phosphoramidothiolates		Methamidophos Acephate

2.3.2 Classification by mammalian toxicity

This is the most widely used form of classification and is certainly the method most understood by farmers in combination with the poison schedules. This form of classification is based upon toxicity testing in mammals and involves oral and dermal testing of the technical product and each active ingredient. The acute toxicity ratings are measured by the LD_{50} method (50% lethal dose). This technique involves the exposure of a randomly selected "named" population to a poison in controlled experimental conditions, and when the mortality rate reaches 50% it is equivalent to the LD_{50}, which is defined in terms of mg/kg (Moretto and Lotti 1993, pp.177–178). These tests are vicarious and the interest is not with the stated, *e.g.* adult male rats but with their extrapolation to human toxicity (Hassall 1990, p.10; Skinner and Kilgore 1982). This type of testing should only be used as a general guide as it cannot identify all risks, *e.g.* a substance with low acute toxicity may be carcinogenic (Moretto and Lotti 1993, p.178; WHO 1988).

TABLE 2.2

Hazard classification of pesticide toxicity

	Rat LD_{50} (mg/Kg body weight)			
	Oral		Dermal	
WHO hazard classification	Solids	Liquids	Solids	Liquids
1a Extremely hazardous	≤5	≤20	≤10	≤40
1b Highly hazardous	5–50	20–200	10–100	40–400
11 Moderately hazardous	50–500	200–2000	100–1000	400–4000
111 Slightly hazardous	>500	>2000	>1000	>4000

2.3.3 Legislative classification

In Australia, pesticides are classified according to a poison schedule, which prescribes the signal headings and labelling requirements for pesticide containers. Anticholinesterase compounds, such as OPs, must be labelled as such. Table 2.3 details the schedules (S) used for agricultural pesticides, their toxicity rating, and the required signal headings (Australian Agricultural and Veterinary Chemicals Council 1989a; Australian Agricultural and Veterinary Chemicals Council 1989b).

TABLE 2.3

Signal headings as specified in the Code of Practice for Labelling Agricultural Chemical Products (1989)

Schedule	Toxicity	Signal Words
S 5	Low toxicity	WARNING KEEP OUT OF REACH OF CHILDREN
S 6	Moderate to high toxicity	1) For internal use CAUTION USE STRICTLY AS DIRECTED 2) For general use POISON NOT TO BE TAKEN KEEP OUT OF REACH OF CHILDREN READ SAFETY DIRECTIONS BEFORE OPENING
S 7	High to very high toxicity	DANGEROUS POISON S7 NOT TO BE TAKEN KEEP OUT OF REACH OF CHILDREN READ SAFETY DIRECTIONS BEFORE OPENING

2.3.4 Pesticide formulations

The formulation of a pesticide refers to its physical form, *e.g.* fumigants, dusts, aerosols, emulsifiable concentrates and wettable powders. Pesticides are usually manufactured from technical grade material, which contains 90–99% of the active ingredient (a.i.) and require dilution and processing into various formulations. The type of formulation governs the availability of the pesticide accessible for occupational exposure. The general components of formulations are given in Table 2.4.

TABLE 2.4

Pesticide formulation components and definitions

Component	Definition
Active ingredient or active constituent	The principal toxic component
Diluents	Inert substances that reduce the concentration of a.i.
Solvents	Liquids such as, water or oils that dissolve the a.i. so that no solids are in suspension (often evaporating after application just leaving the a.i. on the surface)
Surfactants	Detergent like components that are either: 1. emulsifiers that enable oil based pesticides to mix with water 2. wetting agents that enable powder based formulations to mix with water and stay in suspension or improve water based pesticides ability to stick and spread on the surfaces
Synergists	Components that have no pesticidal ability but enhance the activity of the a.i.

Formulations can be pragmatically divided into liquid and solid formulations (Table 2.5).

Table 2.5

Pesticide formulations and descriptions (adapted from Bickford undated, pp.29–31)

Formulation	Description	Comments
	Liquid formulations	
Aerosols	Active ingredient, solvent and propellant	Space and surface spraying
Emulsifiable Concentrate (EC)	Active ingredient, strong organic solvent and emulsifier	Surface spraying and misting
Solution Concentrates	Active ingredient, dissolved in water or alcohol sometimes adjuvants are added	Surface spraying
Suspension Concentrates (flowables)	Active ingredient in a finely milled powder form plus wetting agent	Surface spraying
Ultra Low Volume (ULV)	Technical grade pesticides sometimes with a small amount of spraying oil	Large scale space and surface spraying
	Solid formulations	
Baits	Active ingredient mixed in food or water	
Dry Flowables	Active ingredient that is in a very finely milled form with a small amount of inert carrier and dispersing agent. Forms a suspension when mixed with water	Can be packaged in plastic sachets, or can have adhesive added and compressed as pellets. Surface spraying
Dusts	Active ingredient plus carrier, *e.g.* talc or clay	Seed dressings, surface treatment in dry areas
Granules	Active ingredient plus carrier, *e.g.* talc, clay or inert polymer	Broadcasting through droppers or soil drilling
Pellets	Active ingredient plus carrier, *e.g.* talc, clay or inert polymer	Larger than granules therefore have a greater residual effect
Soluble Powders	Active ingredient and inert carrier must be water soluble	Space and surface spraying
Vaporising Compounds	1. Active ingredient plus slow burning combustible fuel 2. Active ingredient with some vaporising properties plus plastic 3. Active ingredients that react with substances	1. Works on ignition, *e.g.* mosquito coils 2. Works when exposed to the atmosphere, *e.g.* pesticide strips 3. Usually in tablet form *e.g.* fumigants
Wettable Powders (WP)	Active ingredient very finely ground plus wetting and dispersing agents	Surface spraying
Water Dispersible Granules	Active ingredient in granule form	Forms solutions and requires little agitation

There are numerous methods of classifying OP insecticides and only four have been presented in this chapter. It is normal practice to use them concurrently.

2.4 Occupational Exposure

Exposure to a pesticide refers to the deposit of a compound on to clothing without necessarily being absorbed, whereas dose refers to an amount that has entered the body including skin sequestration (Nigg and Stamper 1989, p.6). Exposure routes are customarily described as ingestion, inhalation and dermal. However exposure routes can be concomitant, acute and/or chronic. Occupational exposure to pesticides can occur during manufacturing, processing, transportation and in end use situations. The dermal route is the most critical for occupational exposure (Karr *et al.* 1992).

Measurement of exposure can be classified as biological monitoring and environmental monitoring. Biological monitoring refers to the measurement of parent compounds, their metabolites or an indicator of response in a biological sample such as urine, blood, sweat, saliva and exhaled breath. Environmental monitoring refers to the measurement of ambient levels of pesticide in the worker's environment and passive dosimetry to estimate the quantity that comes into contact with the worker (Nigg and Stamper 1989, p.6). Both methods are now discussed in greater detail enmeshed with some of the health effects experienced by OP exposure.

2.4.1 Biological monitoring

Two common methods for biological monitoring to determine OP exposures include the measurement of blood cholinesterase inhibition and urinary metabolite excretion. Cytogenetic testing is also included in this section although it is less common (Fenske and Leffingwell 1989).

2.4.1.1 Blood cholinesterase monitoring

Historically blood cholinesterase monitoring has been the method of choice for determining OP exposure. There are two distinct types of cholinesterases: erythrocyte cholinesterase (AChE) also known as red cell cholinesterase; and pseudocholinesterase (ChE), which is also known as plasma cholinesterase (Matsumura 1985, pp.507–508). Blood cholinesterase monitoring includes assays of AChE and ChE, which are carboxylic ester hydrolyses that are forcefully inhibited by OPs (Aaron *et al.* 1990, p.680). The popularity of this method arose from the recommendations of the WHO (World Health Organisation) Expert Committee on the Safe Use of Pesticides in 1973 (Bonsall 1985, p.20). The purpose of cholinergic monitoring is to detect OP exposure by measuring depressions in ChE and/or AChE, as many are excreted as non specific metabolites (Hayes 1982, p.304).

The benefits of assessing cholinergic inhibition for the determination of OP toxicity are somewhat doubtful, and are actively being questioned by the scientific and medical communities (Loevinsohn 1987). Nevertheless cholinergic monitoring is still widely practised and many countries have regulations that ensure that commercial pesticide operators have routine blood cholinesterase monitoring (Fenske and Leffingwell 1989). The following section will provide a brief outline of relevant biotransformation and neurotoxicity processes.

2.4.1.1.1 *Esterase classification by organophosphorus compound specificity*
Esterases are both microsomal and cytosolic enzymes. In mammals xenobiotics can be hydrolysed by many non-specific microsomal esterases. Cytosolic esterases are usually associated with particular reactions such as AChE and ChE. Esterases can be broadly classified into three categories according to their reactivity with OPs, A-esterases, B-esterases and C-esterases. There is overlap in substrate specificity and therefore these groupings should not be considered as absolute (DeBethizy and Hayes 1989, p.58; Sipes and Gandofli 1991, pp.88–89). A description of the groupings follows.

A-esterases (arylesterases) use OP esters as substrates. Preference is for carboxylesters with aryl groups in the R position (DeBethizy and Hayes 1989, p.58). Malathion [O,O-dimethyl S-(1,2-dicarbethoxyethyl) phosphorodithioate] is detoxified by A-esterase hydrolysis, esterase cleavage occurs at one or both carbolic esters (Fenske and Leffingwell 1989). Birds and insects have a considerably lower activity of A-esterases than mammals and therefore present a different metabolic profile (DeBethizy and Hayes 1989, p.59).

B-esterases (carboxyl esterases including cholinesterases) are inhibited by OP esters. Preference is for ester alkyl groups in the R position. Most OPs and carbamate insecticides inhibit AChE, which is discussed in greater detail below.

C-esterases (acetylesterases) do not interact with OPs and demonstrate a preference for acetate esters (DeBethizy and Hayes 1989, p.59).

A concise description of acetylcholine (ACh) and its substrate AChE is given in the next two subsections.

2.4.1.1.2 *Acetylcholine*

Acetylcholine is a neurotransmitter used by all motor neurons that innervate skeletal muscle, including gamma-motorneurons, which innervate muscle fibres contained within muscle spindles. Preganglionic neurons in the autonomic nervous system, postganglionic neurons of the para sympathetic nervous system and some postganglionic sympathetic neurons also require ACh as a neurotransmitter. Acetylcholine is also used in the brain by many neurons especially in the basal forebrain (including the nucleus basalis), the Betz cells, which provide one of the origins of the corticospinal tract, and many short axoned neurons in the neostriatum (caudate nucleus, putamen and nucleus accumbens) (Brown 1991, p.74).

Acetylcholine is the only low molecular weight transmitter substance that is not derived from amino acids. The biosynthetic pathway for ACh consists of one enzymatic reaction. Acetylcholine is formed by the acetylation of choline and this reaction is catalysed by choline acetyltransferase. Acetyl coenzyme A is not specific to cholinergic neurons. Choline cannot be synthesised by nervous tissue and it is ultimately derived from the diet (Brown 1991, p.74; Schwartz 1985, p.150).

Acetylcholine is rapidly hydrolysed and removed by AChE in the synaptic cleft. This reaction releases choline that is taken up by the nerve terminals and acetylated to form ACh. Vesicles are synthesised from recycled vesicular membrane and package ACh (Brown 1991, p.76).

Acetylcholine may combine with either muscarinic or nicotinic receptors on the post synaptic cell. Transmitter receptor combinations may lead to a variety of responses (Brown 1991, p.74). Nicotinic manifestations include altered muscle strength in skeletal muscle and fasciculations. These reactions are rapid in onset and of short duration. Muscarinic manifestations include exocrine gland stimulation (copious salivation and bronchi tracheal secretions) and smooth muscle involvement, which results in diarrhoea and miosis (Du Toit *et al.* 1981). Muscarinic manifestations are known by the acronym SLUDGE: *salivation, lacrimation, urination, defecation, gastro-intestinal and emesis.*

2.4.1.1.3 *Acetylcholinesterase*

The term AChE refers to a group of enzymes that hydrolyse to ACh. These enzymes are found in plasma (pseudocholinesterase or butyrylcholinesterase) and in erythrocytes (red blood cell cholinesterase or true acetylcholinesterase).

Pseudocholinesterase is principally a hepatic protein that circulates in the plasma and is also located in the pancreas, heart and white matter of the brain. This enzyme rapidly hydrolyses ACh and other choline esters, including benzocholine, however acetyl-beta-methylcholine cannot be hydrolysed.

Erythrocyte cholinesterase represents the AChE found in the nerve tissue, brain and erythrocytes. Substrates such as butyryl and other acyl thiocholine and choline esters may be acted upon by AChE. Erythrocyte cholinesterase can hydrolyse acetyl-beta-methylcholine but not benzocholine (Aaron *et al.* 1990, p.684; Brock 1991).

Organophosphorus insecticides are highly toxic substances that inhibit ChE and AChE. The mechanisms for these inhibitions are discussed in the next section.

2.4.1.1.4 *Cholinesterase response to organophosphorus challenges*
The majority of OPs are anticholinergic agents, a notable exception being bicyclic phosphates (Matsumura 1985, p.164). Characteristically most OPs emulate the gross molecular shape of AChE, the natural substrate of ACh.

Organophosphorus derivatives act by combining with and inactivating AChE through the formation of stable phosphorylated enzyme complexes (Dreisbach 1983, p.121). In cholinergic synapses there is a surplus of AChE. Generally cholinergic dysfunction is only apparent following an AChE inhibition of 60–90% (Abou-Donia *et al.* 1988, p.9). There are two recognised active sites for ACh; the esteratic site and the anionic site (Matsumura 1985, p.165). Pseudocholinesterase reacts more slowly with ACh because the anionic site is not as suitably positioned (Hayes 1982, p.291). Organophosphorus compounds form a phosphoric acid ester with the enzyme and attack the esteratic site (Abou-Donia *et al.* 1988, p.9). This reaction results in the formation of dimethylphosphoryl enzyme (Ebert *et al.* 1988, p. 670). The rapidity and stability of this reaction is directly associated with the structure of the phosphate ester (Dreisbach 1983, p.121). The phosphorylated enzyme is hydrolysed very slowly and may be irreversible with some compounds. This irreversibility is associated with the loss of one of the alkyl groups that results in a negatively charged monoalkoxyphosphorylated enzyme on the phosphorylated enzyme. This process, which is also pH and temperature dependent, is termed aging (Abou-Donia *et al.* 1988, p.10; Matsumura 1985, p.172).

Unhydrolysed ACh accumulates in the central nervous system (CNS) at autonomic synapses, exocrine glands and motor end plates. The clinical profile is due to

excessive continued action of ACh on muscarinic and nicotinic receptors. Usually muscarinic and nicotinic manifestations coexist (Du Toit *et al.* 1981).

Following exposure to OPs ChE will depress more rapidly than AChE. However, the level of depression of AChE is a more reliable indicator for clinically significant cholinesterase depression (Ames *et al.* 1989; Ebert *et al.* 1988, pp.670–671; Goldfrank 1982, p.285).

Recovery of AChE is limited to the production of new erythrocytes because circulating erythrocytes are incapable of synthesising cholinesterase. Synthesis occurs in erythropoietic cells of the bone marrow (Hayes 1982, p.298). Erythrocyte cholinesterase will take five to six weeks to return to baseline. In an untreated person AChE will increase by approximately 1% per day (Aaron *et al.* 1990, p.685). Levels of AChE are less affected by pathophysiological conditions than ChE (Ames *et al.* 1989). Factors that influence AChE include agents that influence the circulating life of erythrocytes such as haemoglobinopathies and other anaemias (Aaron *et al.* 1990, p.685).

Pseudocholinesterase, synthesised in the liver, will take four to six weeks to return to baseline, having its greatest increase of 25–30% occurring during the first seven days and then will gradually increase (Hayes 1982, p.298). Several studies have observed a rebound effect where the ChE levels are greatly elevated above baseline following a depression (Peoples and Knaak 1982, p.43). Essentially ChE is a hepatic protein and it therefore follows that cirrhosis, malnutrition, neoplasia, infection and other liver dysfunctions plus certain pharmacological agents may affect ChE levels. During pregnancy, particularly the first and second trimesters, ChE levels are depressed (Aaron *et al.* 1990, p.685). Although these influential factors are of some interest to clinicians, it is unlikely that those individuals with depressions associated with pathology will be in the workforce in the developed nations. Thus, it is pharmacological agents, such as opiates and phenothiazines which potentiate ChE inhibition (Peoples and Knaak 1982, p.45) that are more important for occupational studies in Australia.

Furthermore these enzymatic measurements cannot provide a correlation to toxicological or clinical effects (Brock 1991; Goldfrank 1982, p.285; Suber 1989, p.509). Gradual inhibition of cholinesterase from continued low level exposure to OPs is less likely to produce symptoms than the same inhibition from a single large challenge (Aaron *et al.* 1990, p.685; Abiola *et al.* 1991; Chadee and Le Maitre 1991; McConnell *et al.* 1990). Measurement of cholinesterase depression should not be

limited to static measurements, but attention should be paid to the rate of depression. Following chronic exposure to OPs results in depressions to AChE (McConnell *et al.* 1990) and/or ChE (Chadee and Le Maitre 1991), which are not necessarily reflected by clinical observations.

Detection of cholinesterase inhibition ideally should involve the measurement AChE and ChE (Aaron *et al.* 1990, p.684). However, ChE is easier to assay and has been the most frequently used enzyme for health surveillance.

2.4.1.1.5 *Laboratory testing: procedures standards and interpretation*
Historically cholinesterase testing has been an important method for determining OP poisoning and has been extensively used since World War 11. Monitoring procedures have evolved around three complementary methods—research methods, large sampling procedures and smaller fieldwork methods.

Many large scale field studies have confirmed that depression of AChE does not necessarily correlate with symptoms of OP toxicity. An important field investigation took place in Nicaragua during 1984 in order to detect excessive exposure to OPs. It was reported that 8% of a 1,960 sample had low AChE levels. One of the primary conclusions reached in this study was that mass scale AChE monitoring is not feasible. The basis for this is that there was no correlation between reported symptoms and depressed AChE (Cole *et al.* 1988). This finding is not supported by the Cuban experience, where every worker involved with OPs is monitored every three months in conjunction with medical examinations (Alexander and Anderson 1984). Removing asymptomatic workers from the place of work will have a major effect on productivity and may also impose financial hardship. The Cuban infrastructure for occupational health in the rural sector is much more advanced than in Nicaragua.

Several small scale acute poisoning studies have determined that with acute OP poisoning AChE and ChE depression levels are generally lowest at twenty-four to forty-eight hours following the initial exposure (Du Toit *et al.* 1981). Bardin *et al.* (1987) found that clinical recovery could be correlated with AChE improvement but not with ChE or tissue levels of AChE.

In acute poisoning, generally, manifestations only occur when 50% of cholinesterase is inhibited. Mild poisoning occurs when their cholinesterase activity is 20–50% of normal. Moderate poisoning occurs when cholinesterase activity is 10–20% of normal and severe poisoning occurs when cholinesterase activity is less than 10% of normal (Aaron *et al.* 1990, p.684).

The impetus behind the notion of normal cholinesterase levels has evolved from two different approaches. The first approach has been to compare differences in group mean values of exposed workers to control groups (Abiola *et al.* 1991). This approach is frequently the only method available in cases of acute toxicity requiring critical care management (Bardin and Van Eeden 1990; Bardin *et al.* 1987; Du Toit *et al.* 1981).

The second approach has been to compare individual pre-exposure and post exposure levels (Abiola *et al.* 1991). The WHO and the United States National Institute Occupational Safety and Health (NIOSH) recommend that a 30% drop in baseline ChE be considered as decreased ChE activity. This method is a more accurate indicator because interindividual normal range can have an almost twofold increase over the lower limit of "normal". A decrease of well over 30% for someone with a high baseline cholinesterase level would still leave the person in the normal range (Brock 1991; McConnell *et al.* 1990).

Techniques for assessing cholinesterase activity are multifarious. The actual measurement of cholinesterase is rather difficult and usually not done and it is the hydrolytic capacity of the enzyme that is measured (Ebert *et al.* 1988, p.671; Innes *et al.* 1990). Enzymatic methods used are Δ pH, which is measured by electrometric methods, colorimetric methods and titrimetric methods. Physical and chemical assays include immunoassay and high pressure liquid chromatography (Fernando *et al.* 1993).

This diversity of monitoring techniques has unfortunately encouraged individual laboratories to establish their own reporting scales and set of norms (Ames *et al.* 1989; Hayes 1982, pp.304–305). These factors make comparison of studies difficult and do not allow for accurate interpretation. Not only is this a difficulty for researchers but has imposed real hardships on some employees where mandatory ChE testing applies. California provides an apt illustration where operators are required to undergo two tests to provide baseline data, involving a thirty day abstinence from OP exposure. If the operator changes laboratories, *e.g.* with job mobility, he/she is required to provide new baseline data to comply with the regulations in the *State of California Administrative Code, Title 3, Section 2477.* The disparity in measurement techniques also hinders OP poisoning diagnosis, as Californian State Laboratories do not use comparable techniques with State Hospital Laboratories (Ames *et al.* 1989).

Interpretation of decreased ChE activity invites caution. The use of ChE activity measurement for biological monitoring should not be confused with relating the

enzymatic activity to clinical or toxicological effects (Brock 1991). Ethyl OPs, such as parathion, may inhibit ChE more than AChE; whereas the opposite is true for methyl OPs, such as mevinphos (Ames *et al.* 1989). Deliberation is necessary to determine if the reduction is due to a decrease in catalytic activity, or increased ChE degradation or by partial inhibition of the catalytic activity, the latter due to absorbed OPs (Brock 1991).

Enzyme kinetics, inhibition, reversion and replacement, are of particular importance to daily measurements (Popendorf 1990). Cumulative effects have been reported by Baker *et al.* (1978) where ChE levels were highest on Monday and lowest on Friday. Popendorf (1990) noted that there was considerable variability in the daily means of ChE but this variability was markedly decreased toward the end of the season.

Occasionally measurements may be influenced by exogenous factors such as analytical imprecision and human error. Samples may become contaminated, for instance chemical transfer from skin during venipuncture (Brock 1991; Cole *et al.* 1988).

Pseudocholinesterase degrades rapidly and AChE is extremely unstable even at –20°C (Brock 1991). Wagner (1983, p.220) noted that the longer samples were left, prior to freezing and after thawing, the more significant the error. The use of oxalate tubes may provide a false depression in erythrocyte AChE. Preferentially EDTA (Ethylenediaminetetra-acetic acid) tubes should be used (Aaron *et al.* 1990, p.684). These types of errors are rare and are insignificant when compared to the range of cholinesterase levels.

2.4.1.1.6 *Population variance in cholinesterase levels*

There is wide variation in ChE activity in healthy subjects. These variations are independent of electrophoretic heterogeneity and are statistically related to physiological factors such as gender, body weight and mass. Pathological and other physiological factors also have a significant influence (Brock 1991).

Generally females have lower AChE levels than males and this is further reduced with pregnancy and oral contraception. It has also been reported that there are age related differences, although Fuller and Berger (1990) reported that children compared favourably to non pregnant women including those not using chemical contraception. Chadee and Le Maitre (1991) noted that diazepam consumption was responsible for some of the low ChE levels in their control group during a ten year study in Trinidad.

Certain aspects of esterase enzymes are genetically influenced. Biosynthesis of the 574 amino acid subunit for ChE is controlled by the ChE-1 locus on chromosome No. 3 where the genotype is controlled by a number of alleles; ChE^{u}, ChE^{a}, ChE^{f}, ChE^{s}, ChE^{j} and ChE^{k}. In Caucasian populations approximately 2% of individuals present with this atypical trait. Some racial variations have been demonstrated to have a higher incidence for this recessive atypical gene, *e.g.* the Inuits (Brock 1991). Hayes (1982, p.307) noted that genetically atypical ChE individuals were not inhibited by OP exposure and therefore were not subject to toxicity.

2.4.1.1.7 *Disadvantages for blood monitoring.*
There are several disadvantages associated with serum monitoring, and the main ones are briefly mentioned. It is becoming increasingly difficult to obtain authorisation from various bioethics and ethics committees to conduct human experimentation. Human subjects are generally averse to invasive techniques. Many new pesticides are rapidly degraded from blood and it is also virtually impossible to ascertain the initial dose, (Nigg and Stamper 1989, pp.8–9). It is often difficult to maintain extended studies as agricultural workers are often transient.

2.4.1.1.8 *Short review of cholinesterase studies*
The literature is replete with cholinesterase studies. A comprehensive review of the literature, prior to 1982 is provided by Hayes (1982, pp.304–315). This review demonstrates that there is a great diversity in types of studies and results are often in conflict. Another substantial review of pesticides and health effects from 1975–1991 is provided by Maroni and Fait (1993). Some of the more modern trends follow.

Endo *et al.* (1988, pp.565–568) reported that workers exposed to Diazinon® and propaphos, in a Japanese pesticide plant, had significantly lower ChE levels than the control groups while AChE was unaltered. The conclusion reached was that ChE was a more sensitive indicator for Diazinon® and propaphos exposure. Similar findings were reported by Peedicyil *et al.* (1991) in an Indian pesticide plant. In this study the workers were manufacturing malathion, dimethoate and monocrotophos and had been in the work force from three months to thirty-two years without using any PPE. The mean ChE levels of the exposed workers were within the normal range limits, although their levels were much lower than the control group. There was no correlation between depressed ChE and duration of exposure. Some of the exposed workers exhibited signs of peripheral neuropathy.

In a comparative study of fenitrothion as an EC applied by ULV it was reported that AChE was depressed more by ULV application. It was postulated that vegetable oil

and water-oil mixtures were used for ULV application and that these carriers could penetrate erythrocyte membranes facilely (Abiola *et al.* 1991). Unfortunately, this study did not compare application techniques and therefore the above assumption although plausible, cannot be verified.

A seasonal study of orchard workers using a variety of OPs reported that estimated dermal exposure correlated well to a decrease in AChE but not to ChE. None of the applicators had clinically significant decreases in AChE or ChE, but because of the subclinical changes, these researchers suggested that acute low dose exposure may be determined by AChE (Karr *et al.* 1992).

Studies that examine continued low levels of exposure to OPs are not as prevalent as short term seasonal studies.

Urine monitoring is particularly important in cases of acute exposure and is discussed next.

2.4.1.2 Urinary metabolites

The main urinary metabolites formed from OPs are dialkyl phosphates, which are a more sensitive indicator of OP absorption than cholinesterase inhibition, although urine and serum testing are usually done concomitantly (Waldron 1988, p.77). The most common metabolites are: O,O-diethyl phosphate (DEP); O,O-dimethyl phosphate (DMP); O,O-diethylphosphorothionate (DETP); O,O-dimethyl phosphorothionate (DMTP); O,O-diethylphosphorodithioate (DEDTP); and O,O-dimethylphosphorodithioate (DMDTP) (Weisskopf and Seiber 1989, pp.206–207). Analysis is by gas chromatography and various techniques are reported in the literature (Fenske and Leffingwell 1989; Lavy and Mattice 1989, pp.198–200; Moody *et al.* 1985; Weisskopf and Seiber 1989, pp.206–207).

Analyses of urinary metabolites are somewhat complicated because specific analytical methods are required for each exposure. Some studies suggest that analyses of urinary metabolites can determine the amount of pesticide that has been absorbed (Dubleman and Cowell 1989; pp.240–250; Weisskopf and Seiber 1989). O,O-dimethyl phosphorothionate was not found to be dose dependent in people applying guthion (Stokes *et al.* 1995). However, there are inherent differences in excretion rates that are attributed not only to the quantity of the compound absorbed but by the retention in the body (Drevenkar *et al.* 1993; Vasilic *et al.* 1992). Urinary metabolites from sheep dippers were found to be a more sensitive indicator than serum analysis but were non-specific. There was no relationship between the concentration of urinary

metabolites, date of dipping, the quantity of OPs used, the number of sheep dipped and reported exposure and/or work practices. This study did not find any evidence of acute OP exposure in sheep dippers (Rees 1996).

2.4.1.3 Cytogenetic testing

Cytogenetic testings on human somatic cells are customarily used for early assessment of exposure to mutagenic and carcinogenic agents. The two types of abnormalities that are usually examined are chromosome aberrations (CA) and sister chromatid exchanges (SCE). Chromosome aberrations are performed *in vitro* on peripheral blood lymphocyte cultures. A review of genetic damage by these methods by Maroni and Fait (1993) suggests that these tests are too inconclusive to establish specific pesticide exposure. Within the literature there is no consensus for pesticide exposure and increased frequencies of SCE, as there are many confounding factors. Carbonell *et al.* (1990) found no difference in SCE between pesticide exposed workers and control groups, although the smokers had higher frequencies of SCE than non-smokers. Malathion has been shown to increase CA and be dose dependent (Garry *et al.* 1990). More recent research has provided evidence associating malathion exposure to human T cell mutations (Pluth *et al.* 1996). *In vivo* testing of technical grade malathion in animal studies has demonstrated CA, while *in vitro* studies of animal and human cells produce SCE and CA (Flessel *et al.* 1993).

Spray operators who had used a variety of pesticides had significantly higher rates of CA than the control group. Greenhouse workers who used benomyl had significantly higher frequencies of CA forty-eight hours post application, although this had reverted one year later (Desi *et al.* 1990). A comparative study of Indian male pesticide applicators found that there were significant increases in SCE and cell cycle delay in the pesticide users. A variety of pesticides were used in this study and confounding factors such as X-ray exposure, alcohol and smoking were eliminated (Rupa *et al.* 1991).

2.4.2 Health effects unrelated to acute cholinesterase inhibition

Organophosphorus compounds are also able to gradually phosphorylate a number of other enzymes that include: acid phosphatase; aliesterases; lipases; trypsin; chymotrypsin; succinoxidase; ascorbic acid oxidase; dehydrogenase; and sulfhydryl (Hayes 1982, p.291).

Many of the lipophilic OPs readily cross the blood brain barrier. Two principal constituents of biological membranes are phospholipid and cholesterol, the former being crucial for AChE mechanisms. *In vitro* studies of malathion and phosphamidon

demonstrated that there was an altered substrate binding capacity. It was also suggested that variations in lipid structure and composition appear to influence the specific effects of insecticides on AChE activity (Datta *et al.* 1994). Abiola *et al.* (1991) noted that there was no correlation between lipid and lipoprotein metabolism to depression of ChE.

Srivastava *et al.* (1991) conducted a study in northern India on dusshery (a type of mango) orchard workers who were using a variety of pesticides including carbamates, organochlorine insecticides and OPs, and, as expected, ChE levels were depressed. However, serum alkaline phosphatase was significantly elevated in exposed individuals and slightly higher in those individuals with a ten year work history. These findings are indicative of hepatic involvement. These workers wore little or no protection and their general health status was poor. This finding was supported by an Egyptian study of OP sprayers that identified elevated glutamic pyruvic transaminase and serum alkaline phosphatase in the sprayers and not in the control group. Their conclusion was that long term exposure to OPs resulted in hepatic effects (Kamal *et al.* 1990).

Osteoporosis and osteopenia were associated with OP exposure in farmers, in a small British pilot study. It was postulated that the phosphate groups bind to calcium on the bone surface. This is currently the topic of a much larger study (Day 1997).

A few studies have reported haematological toxicities, *e.g.* aplastic anaemia, and leukaemia (Jenkyn *et al.* 1979; Lorand *et al.* 1984; Reeves *et al.* 1981). These have been typically reported as case studies and involve other pesticides.

The principal conditions following acute cholinesterase inhibition are intermediate syndrome and organophosphate-induced delayed polyneuropathy (OPIDN), which are briefly discussed below.

2.4.2.1 Intermediate syndrome

Intermediate syndrome is associated with: fenthion and its analogues; diclofenthion and fenitrothion; dimethoate; monocrotophos; methamidophos; diazinon; and malathion. It occurs twenty-four to ninety-six hours after an acute cholinergic crisis (De Bleecker *et al.* 1992b; Senanayake and Johnson 1982) and is manifested by muscle weakness, particularly those innervated by the cranial nerves (Ecobichon 1991, p.582). The duration of these signs can be from days to weeks and paralysis of the respiratory muscles can occur if untreated (De Bleecker *et al.* 1992a; Karademir *et al.* 1990). De Bleecker *et al.* (1992b) found that parathion in combination with methyl

parathion was more likely to induce intermediate syndrome rather than parathion alone. Their conclusions were that the syndrome resulted from prolonged end plate esterase inhibition and electromyography tests demonstrated pre and post synaptic dysfunction at the neuromuscular junction. Tentative factors that predispose to intermediate syndrome are the high lipid solubility of some OPs, impaired cardiovascular systems and renal and/or hepatic systems which in turn prolong metabolism of toxicants (De Bleecker 1995).

2.4.2.2 Organophosphate-induced delayed polyneuropathy

Several weeks after OP intoxication there may be a sensory motor peripheral neuropathy stage known as organophosphate-induced delayed polyneuropathy (OPIDN). This is characterised by a Wallerian type degeneration of the long myelinated nerve axons, in particular the sciatic nerve and spinal column, and is manifested by hyporeflexia, distal numbness, paraesthesia, ataxia and weakness (Chambers 1992, p.14). Organophosphate-induced delayed polyneuropathy is classified as Type 1 and Type 11. Type 1 is induced by all OPs except the phosphites, which produce Type 11 (Abou-Donia 1992, pp.331–335). The distinctive features of Type 1 are muscarinic signs, whereas Type 11 are similar to the intermediate syndrome (De Bleecker 1995).

Neuro target esterase (NTE), a protein of the nervous tissue, has an effect upon lipid metabolism in neurons. Prior to the development of OPIDN there is at least a 70% deactivation, or aging, of NTE with strong neuropathic agents, 80–90% with moderate neuropathic agents and 100% with the weakest agents (Lotti *et al.* 1993). Organophosphorus compounds that act as non agers will protect against OPIDN if administered immediately before the aging compound, although if given soon afterwards may enhance the neuropathic potential of the agers (Kaplan *et al.* 1993). Neuro target esterase is the accepted biomarker for OPIDN and is tested upon the most susceptible species, the hen and cat (Ecobichon 1991, pp.583–584). However, not all known OPIDN inducing agents produce the same reactions within species (Kinebuchi and Nishiyama 1987). There is a wide range of interindividual variation of NTE in an unexposed population and therefore this method can provide qualitative data only (Mutch *et al.* 1992).

Chlorpyrifos caused reversible distal symmetric neuropathy and mild cognitive dysfunction as reported in case studies (Kaplan *et al.* 1993)

2.4.2.3 Chronic neurological effects

Few studies have examined chronic neurologic sequelae following OP exposure. Ames *et al.* (1995) explored this area with sub-acute poisoning in agricultural pesticide operators and suggested that prevention of acute poisoning acts as a prophylaxis against chronic neurologic sequelae. Organophosphorus poisoning sequelae that have been identified include toxic encephalopathy (Rosenstock *et al.* 1990).

2.4.2.4 Neuropsychological studies

The neurobehavioural effects observed following intoxication by OPs include anorexia, difficulty in concentration, memory impairment, ataxia, muscular weakness, decreased reaction time, emotional lability, anxiety and confusion (D'Mello 1993). A review of neurobehavioural effects caused by OPs concludes with a caution that these compounds can have a detrimental, long lasting and possible irreversible effects that have been demonstrated across all species and all ages (Annau 1992, p.429). Earlier reviews suggested that there needed to be more rigorous research in this field as there were limitations due to the inability of quantifying the exposure, the multiplicity of pesticides used and problems with the actual testing procedures. However, there was enough evidence to suggest that chronic exposure to pesticides leads to adverse health effects (Davies 1990; Rosenstock *et al.* 1990).

A neurobehavioural study of workers applying diazinon in granule formulations did not find any relationship between exposure and behaviour (Maizlish *et al.* 1987). A comparative prospective longitudinal study between apple orchard workers and slaughterhouse workers, over one season, failed to find any evidence of neuropsychological performance inhibition (Daniell *et al.* 1992). Rosenstock *et al.* (1991) performed neuropsychological assessments on a group of Nicaraguan males, and a control group, two years after OP intoxication. There were no baseline data or exposure duration recorded, although their findings revealed that the exposed group performed much worse than the control group in a battery of tests.

In more recent times a study was conducted on British sheep farmers who had used OPs for sheep dipping. Quarry workers participated as a control group and the testing procedures involved computer assisted psychological tests and questionnaires. The sheep dippers performance was much worse in sustained attention and in speed of information processing (Stephens *et al.* 1995).

2.4.2.5 Dermatoses and sensitisation

Many pesticides are the causative agents for dermatoses such as erythema multiform, toxic epidermal necrolysis, chloracne, porphyria cutanea tarda and discolouration of the hair and nails. Allergic dermatitis from OPs is rare, although there have been some documented cases from exposures to parathion and malathion (Sharma and Kaur 1990).

A chemical that acts as a sensitiser induces a cell-mediated hypersensitivity reaction. The sensitising chemical permeates the epidermis and reacts with proteins to form hapten. Antibodies are produced against hapten and when the same chemical is applied severe and acute reactions occur, *e.g.* erythema, oedema and development of vesicles. Malathion has been recorded as a sensitising agent (Ness 1994, pp.27–28). Sensitising chemicals can be leached from protective shoes and rubber gloves (Tucker and Key 1983, p.308).

Due to the importance of dermal exposure in the occupational setting an abridged description of anatomical and physiological details that constitute the barrier properties of the skin are detailed in the next section.

2.5 Barrier Properties Of The Skin

The skin acts as a barrier between the body and pesticides. It is the largest organ of the body comprising 15% of the total body weight with an approximate surface area of nine square meters in an average sized adult (70 Kg). The skin consists of three major strata: the epidermis; the dermis; and the hypodermis. Anatomically, there are regional variations in the thickness, number of appendages and follicles. Each layer exhibits some barrier properties.

The epidermis is the major barrier to non-traumatic cutaneous disease. Normally it is thin (about 0.12 mm thick) but thicker in areas subject to pressure or friction, *e.g.* soles of the feet. It consists of four or five layers: the stratum corneum; the stratum lucidum; the stratum granulosum; the stratum spinosum; and the stratum basalis. The stratum corneum is the most superficial layer of the epidermis. It consists of flat, densely packed dead cells called corneocytes whose cytoplasm has been replaced with the insoluble protein, keratin. These cornified cells cover the entire body providing a water resistant barrier and restricting the loss of body water. The use of organic solvents or other chemicals, which are lipophilic, and the use of strong detergents can disrupt the stratum corneum. The living epidermal cells can be exposed to xenobiotics if the integrity of the stratum corneum is impaired. Permeation of xenobiotics through the stratum corneum involves sorption at the external surface of the stratum corneum

followed by diffusion and desorption into the circulatory system of the epidermis and dermis. The stratum lucidum is only found in the thick skin of the palms and soles. It consists of eleidin, which ultimately transforms to keratin, and clear flat dead cells. The stratum granulosum is composed of three to five rows of flattened cells containing keratohyalin that is required for keratin formation. The stratum spinosum is composed of eight to ten rows of polyhedral cells. Merkel's discs, nerve endings with tactile sensitivity, are contained in this layer in hairless areas. The stratum basale consists of a single layer of cuboidal or columnar cells, which are able to sustain continual cell division. This allows for the cells to push upward and they are integrated into the other layers (Tortora and Anagnostakos 1987, pp.103–104).

The dermis consists of dense irregular connective tissue approximately 2 mm thick and has a considerable supply of blood vessels, nerve cells and lymph vessels. The dermis is of variable thickness being thicker on the palms and soles and thinner on the eyelids, penis and scrotum. Generally there is a tendency towards thicker regions on the dorsal integument and lateral aspects of the extremities. It contains specialised sense organs and glands. There are two sections to the dermis, the papillary region and the reticular layer. The papillary layer contains structures which project into the epidermis, some of which contain capillary loops. The reticular layer consists of tightly laced collagenous and elastic tissues.

The hypodermis attaches the skin to the underlying structures and is well supplied with nerve endings, blood vessels and subcutaneous fat cells. It acts as an insulator and has cushioning properties (Tucker and Key 1983, pp.301–303).

The epidermal appendages incorporate both the eccrine and apocrine sweat glands, hair follicles and sebaceous glands. The sweat glands are distributed over most of the body except for the hairless regions, for instance, the palms of the hands. Stimulation of the sympathetic nerves causes them to secrete a watery solution consisting of sodium chloride, with traces of urea, sulphates and phosphates (Tortora and Anagnostakos 1987, pp.101–103). Compounds that are highly polar can readily permeate the skin through the pores in the epidermal appendages (Schwope 1986). However, diffusion through these pores is considered to be a minor route of penetration (Emmett 1991, p.466). Increasing skin temperature is associated with an increase in rashes and this is thought to be due to increased sweating that accumulates on the skin surface and acts as a trapping vehicle for some pesticides. As well the pores are more widely open and this may facilitate penetration of the pesticide (Winter and Kurtz 1985).

The skin is a highly active metabolic organ and possesses many of the same enzymes as does the liver. The rate of percutaneous absorption of pesticides is dependent upon the condition of the skin, the anatomical site, the area of exposure, the skin temperature, the nature of the compound and the duration of exposure. Lipophilic compounds readily penetrate the stratum corneum, *e.g.* OPs. Other compounds that are both lipophilic and hydrophilic are more rapidly and completely absorbed (Legaspi and Zenz 1994, pp.617–619). Polar compounds require a hydrated stratum corneum so that diffusion can occur, whereas non-polar compounds diffuse through the lipid matrix (Emmett 1991, pp.455–467). Some pesticides, such as paraquat do not readily penetrate the skin unless there is some damage (Smith 1988). Therefore, hydration of the stratum corneum is a major constituent for skin absorption and this is discussed in detail in Chapter Three.

Post exposure factors play an important part in the pesticide absorption profile. Pesticides reside on the skin prior to diffusion into the skin and therefore removal of the pesticide, *e.g.* by hand washing, is time dependent. Factors that are involved include the soap and solvent interactions and the amount of vigorousness of the rubbing (Wester *et al.* 1992). Some solvents will enhance the pesticide uptake into the skin (Wester *et al.* 1990). In some cases, washing contaminated skin with soap and water releases pesticides that are entrapped in a dermal reservoir and the washing procedure spreads the pesticide over a greater surface area, thus increasing exposure and absorption potential (Moody and Nadeau 1993). In an *in vitro* study, parathion and malathion had a greater rate of absorption and a greater reservoir affinity than carbaryl or lindane (Chang *et al.* 1994).

The mechanisms of percutaneous absorption are complex processes and are succinctly presented in Table 2.6.

TABLE 2.6

Mechanisms of percutaneous absorption
(adapted from Wester and Maibach 1989, p.136)

Primary mechanism	Sub-sections
Vehicle release	
Absorption kinetics	1. skin site of application 2. individual variation 3. condition of the skin 4. occlusion 5. pesticide concentration and surface area 6. multiple applications
Excretion kinetics	
Cellular and tissue distribution	
Substantivity (non penetrating surface adsorption)	
Wash and rub resistance	
Volatility	
Binding	
Anatomical pathways	
Cutaneous metabolism	

2.6 Environmental Monitoring: Dermal Exposure

The dimension of dermal exposure is a factor of the type of pesticide and formulation, the task in hand, the duration of exposure, the method of application, the knowledge and experience of the operator and adventitious situations. The type of formulation allows for the quantity of pesticide available for dermal contact. Weisskopf *et al.* (1988) found that a granule formulation of diazinon applied by various hand-held apparatuses resulted in very low dermal exposures, although respiratory exposure was much higher and it was suggested that this was because diazinon resided in the operators' coveralls and exposure time was prolonged until they undressed. When dusts are applied the respiratory route is more important than the dermal route (Stevens and Davis 1981). In a small study of vegetable growers applying nitrofen (2,4-dichlorophenyl *p*-nitrophenyl ether) as an EC or as a WP it was reported that those using the WP formulation presented with greater exposure levels (Putman *et al.* 1983).

Tasks can be generally divided into those associated with application and those associated with harvesting or re-entry into a treated area (Fenske 1991, p.340). The

task is an extremely important factor, *e.g.* during mixing and loading, the operator faces a higher risk as he/she is dealing with undiluted pesticides (British Agrochemicals Association 1984). This has been supported by several studies (Everhart and Holt 1982; Krieger *et al.* 1990; Pomorska and Majczakowa 1995). The means of application has a significant effect upon exposure and dermal deposition patterns (Weisskopf *et al.* 1988). London (1994) reported that knapsack sprayers and tractor drivers had potentially the greatest risk of exposure. Pomorska and Majczakowa (1995) found that tractor drivers received less exposure than feeder operators. In a three-way comparative study of helicopter crews, tractor crews and knapsack sprayers applying 2,4,5-T, the knapsack sprayers suffered from considerably higher exposure levels (Lavy *et al.* 1980).

The location of the task is another consideration, *e.g.* workers in green-houses have less room to move and the atmosphere is maintained to ensure optimum conditions for the plants. Consequently, vapours and mists can remain in the air for considerably lengthy periods thus presenting the worker with prolonged atmospheric exposure times (Nazer and Clark 1983). Exposure related to re-entry into a treated area is directly related to the height and density of the foliage and the time of re-entry (Pomorska and Majczakowa 1995). Various engineering controls and methods have been devised to reduce operator exposure, *e.g.* closed cab tractors, boom height and PPE (Hunt *et al.* 1985; Machado Neto *et al.* 1992). However, inspite of these advances dermal exposure continues to be a major problem (Krieger *et al.* 1990).

Dermal exposure can be either direct or indirect. Direct contact can be due to splashes and spills and by diffusive contact from spray droplets or vapour. Indirect contact can occur after contact with contaminated foliage or surfaces (Brady *et al.* 1991). Furthermore, surfaces can be contaminated by splashes, spills, surface to surface contact and diffusive deposition of airborne droplets or dusts. Once deposited and dried these particles can be resuspended and therefore inhalation exposure may occur. Surface to surface contact has been described as the most likely pathway for dermal exposure (van Hemmen and Brouwer 1995; Yoshida *et al.* 1990), although this is time limited as the exposed surface may bind the pesticide irreversibly and/or the pesticide may degrade into non-detectable or undetected products (Ross *et al.* 1991). In a greenhouse study, which only used one subject, hand exposure was thought to be primarily due to contact with contaminated machinery (Stamper *et al.* 1989).

2.6.1 Assessment of dermal exposure

There are several methods used for assessing dermal exposure and there is general agreement in the literature that the hands are the most exposed anatomical region (Abbott *et al.* 1987; British Agrochemicals Association 1984; Fenske 1988b, p.634; Kamble *et al.* 1992; Putman *et al.* 1983) although this is not an absolute finding (Fenske 1991, p.389).

Potential dermal exposure refers to the amount of pesticide that is deposited on the skin, clothing and/or protective equipment, that is, the amount of pesticide that would reach the skin in the absence of this protective equipment. Actual dermal exposure refers to the amount of pesticide that reaches the skin surface and is available for absorption (van Hemmen and Brouwer 1995; Findlay 1995, p.viii).

2.6.1.1 Patch methods

Early methods of assessing dermal exposure involved placing gauze patches on the exterior surface at specific locations on the applicators' clothing and on the interior surface (Durham and Wolfe 1962). The exterior placements were intended to simulate pesticide residues landing on the clothing thus representing potential exposure, and the interior patches represent actual dermal exposure. These pads were subjected to extraction methods and extrapolation of that data to the entire body (Karr *et al.* 1992). This technique was used in a comparative study of applicators using tractor operated or drawn rigs and knapsack sprayers, which determined that legs were the most exposed anatomical site for the knapsack sprayers followed by hands. As well hands were the most significant sites for all tractor driven rigs (British Agrochemicals Association 1984). Putman *et al.* (1983) used this method and reported that hands received the greatest potential exposure and that the protection provided by natural rubber gloves reduced the actual exposure by factors up to 300:1. A substantial limitation of this method is that there is an underlying assumption that there is no clothing permeation of the pesticide or that only 10% will penetrate (Fenske 1991, p.389).

Another underlying assumption is that dermal deposition is uniform whereas in reality it is not. A comparative study of greenhouse applicators reported that the results of patch techniques indicated very heavy exposure, which was not supported by video imaging analysis (Methner and Fenske 1994a). There was further evidence of this in a smaller follow up study (Methner and Fenske 1994b). Mestres *et al.* (1985) conducted an earlier greenhouse study that examined re-entry situations by using absorbent pads, underneath the workers' clothing, and glove monitors. They found high exposures on the hands and lower legs and concluded that PPE was necessary with the compounds they were testing. Lavy *et al.* (1980) suggested that heavy

exposure may have been due to workers rubbing their hands on their thighs to dry them off rather than direct exposure. Additionally there is an assumption that the levels extracted from the patches are accurate representations of exposure (Fenske 1990). Kamble *et al.* (1992) reported that the penetration of insecticides through workers' clothing was much higher in field conditions than in laboratory simulations because of the movements of the workers, whereas (Lavy *et al.* 1993) reported that this technique overestimated real exposure. It boils down to whether or not a representative "dose" reaches the target patch.

Water sensitive paper has been used to assess potential dermal exposure in knapsack sprayers in field conditions with the boom at two different heights. The papers were worn at regular spacings on the ankle, calf, thigh, and forearm on the right side of the body, which had more contact with the boom. Analysis was done using a colony counter. The lower setting of the boom resulted in most of the exposure occurring below the knees whereas the higher setting resulted in exposure moving higher up the body (Lengerich and Burroughs 1989). This method has limited use as it has the same limitations as the patch method. However, the operator is able to see the exposure immediately and it could be used in operator training situations.

2.6.1.2 Glove monitoring

Glove monitoring has been used to assess harvesters' hand exposures. This involves wearing cotton gloves for a specific task and then analysing tracer pesticides from the glove. Superlative descriptions of these techniques are summarised by Ness (1994, pp.346–349) and van Hemmen and Brouwer (1995). A re-entry study for strawberry harvesters for benlate exposure used this method in conjunction with dermal patches and reported that hand exposure was the most significant site in all workers (Everhart and Holt 1982).

A comprehensive NIOSH Health Hazard Evaluation report examining floriculture and nursery products evaluated hand exposure to diazinon by using glove monitors. The results of this study pointed out that wearing latex gloves provided adequate protection for personnel handling treated foliage, which proved to be a serious source of contamination for un-gloved hands (NIOSH 1993). Hand exposure was significantly reduced by wearing rubber and/or PVC gloves in industrial pesticide applicators. However, this was a limited section of a larger study and conclusions can only be tentative as there were only two un-gloved applicators (Popendorf *et al.* 1995).

However, validity of these methods is uncertain and several studies have found that cotton glove monitors gave higher exposure estimates than hand rinsing (Davis *et al.* 1983; Fenske *et al.* 1989).

2.6.1.3 *In vivo* and *in vitro* studies

In vivo and *in vitro* studies have been conducted for combined skin and material barrier experiments. *In vivo* studies involve human and animal studies, there being several models for extrapolation of animal data to the human responses (Hixon 1989). *In vivo* studies on selected animal species, which involve bioassays from percutaneous absorption experiments, have been developed to encompass glove permeability. Boman and Wahlberg (1986) compared the permeation of three organic solvents through three different types of CPGs made of polyvinyl chloride, butyl, latex rubber, with the unprotected skin of guinea pigs for six continuous hours of exposure. Analysis involved gas chromatography of whole blood withdrawn from the carotid artery. Their results suggested that polyvinyl chloride and butyl did provide a limited barrier to dermal absorption of the solvents particularly during the first hour, whereas latex was ineffective. Cotton knit gloves of various weights have been found to provide a protective function against OP dermal absorption *in vitro*. This type of research can be applied to those people involved in harvesting work (Keeble *et al.* 1993). In a human study of percutaneous absorption of diazinon the forearm and abdomen were used to deliver radiolabelled diazinon in two separate vehicles, acetone and lanoline. The absorption ranged from 2.87–3.85% (n = 6) and there were no significant differences found between sites or vehicles (Wester *et al.* 1993).

2.6.1.4 Dye and fluorescent tracers

Tracer dyes have been used to track dermal deposition patterns by adding them to pesticide formulations, or used alone as surrogates and then quantifying the dye retrieval. The surrogate technique was used in an interesting cross cultural study that incorporated four countries in tropical climates with several types of crops. Deposition patterns varied according to the height of the crop (Ambridge *et al.* 1990). A small study of lawn care specialists who used hand spray guns in a dye surrogate method found that the more experienced applicators had greater spray deposition patterns than the inexperienced candidates. This somewhat surprising result was attributed to the greater speed of the experienced applicators who were driven by economical concerns rather than safety concerns. Exposure was greatest on the lower legs followed by the hands (Slocum and Shern 1991).

Fluorescent tracer analysis involves blending a non-toxic fluorescent compound with the pesticide mixture followed by application through normal work procedures.

Immediately after spraying has finished the workers are examined under a long wave ultraviolet light thus obtaining visualisation of the exposure. A video imaging technique for assessing exposure is achieved by using a television camera linked to a microcomputer system that detects and quantifies skin fluorescence. An exposure index has been designed for quantification of various anatomical sites (Fenske *et al.* 1985, p.378). This technique was used on orchardists using air blast sprayers to apply diazinon, run simultaneously with patch tests, personal air sampling, rig sampling and tests to determine the stability of the tracer outdoors. The patch samples indicated that exposure was greatest on the chest whereas the fluorescent tracer technique results were more variable. The two techniques were not comparable. In another study of combined patch and fluorescent tracer analyses, which focussed on the relationship between malathion and the tracer penetration through work shirt and coverall material, it was reported that in both cases malathion penetration was greater in both fabrics. The tracer did not penetrate the coverall material very well, thus highlighting one of the limitations to this research (Fenske *et al.* 1986). In this study and others there were exposures caused by the gap or movement between the top of the glove and the sleeve. A comparative study of orchard airblast operators using malathion and greenhouse workers using a fungicide in handguns determined that orchard workers had an exposure gradient of the forearm, probably due to aerosols or spray being drawn under the protective clothing, whereas the main exposure for the green house workers was on their legs (Fenske *et al.* 1990). Airblast operators and mixers using malathion and standardised PPE had exposure to protected skin, which represented more than 75% of dermal exposure (Fenske 1988a). Airblast operators and mixers showed hand exposure when wearing neoprene gloves, but gloves were taken on and off several times during the study time according to normal work conditions (Fenske 1988b, p.634).

Fluorescent tracer analysis followed up with skin swabbing of the visually contaminated areas by fluorometric analysis was used in a study on airblast operators. These researchers reported that the majority of exposures occur on the hands and head. This study involved only a small number of operators and there was no consistency in the type of PPE used. Most workers wore latex gloves; a few wore leather or butyl and one had naked hands (Karr *et al.* 1992).

2.6.1.5 Skin wiping

Skin wiping techniques involve wiping the contaminated skin with solvent or water moistened swabs, followed by extraction and analysis. This technique has not been very popular because of non-compliance within the subject group particularly when large surface areas, *e.g.* torsos, are to be swabbed. When it is confined to the hands

there is greater compliance. However, it is cumbersome to remove residues from the fingernails and digit interstices.

2.6.1.6 Hand rinsing

The handrinse technique has been accepted more favourably. This involves placing the contaminated hand in a bag that contains a given amount of solvent, clasping the opening tightly around the wrist followed by vigorous agitation for a specified time. The solvent mixture can then be analysed (Findlay 1995, p.ix). The choice of a suitable solvent is paramount, since it must not cause damage to the skin and must not interfere with the analysis (Davis *et al.* 1983). In an assessment of different types of hand-wash techniques it was reported that standard methods were inaccurate and prone to underestimation of actual exposure (Fenske and Lu 1994). This technique was used in a study that compared exposure levels of the herbicide EPTC (S-ethyl-N,N,-dipropyl thiocarbamate) between mixers/loaders, applicators and maintenance operators. The applicators and maintenance workers had much higher levels of hand exposure. The mixer/loaders wore rubber gloves and the applicators had bare hands, although it is not stated what the maintenance workers wore (with the high levels of exposure one assumes that they also had bare hands). Interestingly, but irrationally, these researchers precipitately conclude that the wearing of rubber gloves during mixing and loading and during nozzle cleaning operations enhanced EPTC absorption (Knaak *et al.* 1989).

A combination of the handrinse and patch methods was used in a study of workers in a seed treatment plant. Exposure levels were not detectable on the chests or forearms of the workers when the detection limit was 0.5 mg. However, hand exposure was high in half of the workers (Grey *et al.* 1983). A substantial study that examined exposure to nursery workers to multiple pesticide exposures for a year incorporated dislodgeable residues from seedlings, patch, handrinse and urine methods. The frequency of positive samples was highest in the dislodgeable residues followed by patch, handrinse and urine, although the detected levels were very low and there was no perceived health risk (Lavy *et al.* 1993).

Yoshida *et al.* (1990) found that hands and thighs down to shins were areas of high exposure for tractor boom spray operators and hands and chest for aerial spraying pilots. It was also noted that operators removed gloves after mixing/loading or making adjustments in the field thus enhancing their contact with contaminated surfaces. The scientific method chosen for this study incorporated surface wipes from contaminated surfaces and analyses of tracer pesticides coupled with direct observation.

2.7 Chemical Protective Clothing

Chemical protective clothing provides the last line of defence against exposure to pesticides for farmers. There is a vast array of CPC available in the market place, from gloves to fully encapsulated gas tight suits (Forsberg and Mansdorf 1993, p.2). Selection of CPC is based upon the permeability to a specific chemical. Other factors that warrant consideration are fit, cost, comfort, and physical properties, *e.g.* tear resistance, elasticity, puncture resistance and compatibility with other items of PPE. However, selection of suitable CPC is difficult for the lay person as frequently the polymer is not named on the garment (Airey 1990; Watterson 1988, p.57).

There is no clothing that will resist permeation or penetration indefinitely. Ordinary work coveralls are unsuitable for pesticide application as spray deposition that settles on the seams gradually seeps through. Various patterns for CPC have been tried and include coveralls, trousers, blouses, overboots, gloves, aprons, bib-aprons and cloaked hoods (for use with knapsacks). The design is important, *e.g.* placement and protection of zips. Coated and unbreathable fabrics are superior to uncoated and breathable fabrics. However, these fabrics impede evaporation from the skin and consequently heat stress becomes a problem.

It is beyond the scope of this thesis to give a detailed account of CPC. Comprehensive reviews of CPC are available in the technical literature (Airey 1990; Branson and Sweeney 1991; Faull 1990; Gilbert and Bell 1990; Taylor 1990). The use of CPGs is discussed in the next chapter.

2.8 Chapter Summary And Conclusions

This chapter has briefly explored the evolution of pesticides from the earlier period when only natural products were used through to the present day with the use of modern synthetic chemicals. Four systems of pesticide classification based on chemical, toxicity, Australian legislative and formulation have been broadly described.

The OPs are the most popular class of insecticides in the world because they are extremely versatile, generally they are non persistent in the environment and they are very efficacious insecticides. The main problem is their mammalian toxicity and therefore they provide an occupational risk to farmers and agricultural workers. Neurotoxicity is the major toxicological problem. Acute toxicity responses to OPs involves the inhibition of AChE, which can be life threatening. Delayed toxicity responses include intermediate syndrome and OPIDN. Less severe forms of neurotoxcity have been reviewed which included behavioural and psychological studies.

Dermal exposure is the most common route for occupational exposure to pesticides and the skin anatomy and barrier properties have been described. There are many methods of assessing dermal exposure ranging from absorbent pads, tracer and fluorescent dyes and skin wiping methods, all of which have their limitations. In spite of all the different methods there is general agreement in the literature that hands are the most exposed anatomical region and therefore the importance of CPGs cannot be underestimated. Chemically protective gloves are used to protect the hands from pesticides and this is the topic of the next chapter.

Chapter Three

Polymeric And Elastomeric Materials Used In The Manufacture Of Chemically Protective Gloves: Description And Evaluation Of Contemporary Testing Procedures

3.1 Introduction

Chemically protective gloves are a crucial part of protective apparel for agricultural workers who may be exposed to toxic agricultural chemicals. Such gloves must meet several criteria to be suitable for farmers needs—they must be cost effective, provide adequate protection and be comfortable (Engle and Nusbaum 1984; Mansdorf 1994).

Chemically protective gloves used in the agricultural sector are manufactured from polymeric and elastomeric materials. It is therefore pertinent to discuss some attributes of these materials. The first section (3.2–3.3) of this chapter will review the relevant polymer chemistry. The next section (3.4) examines some relevant types of polymer failure. The final sections (3.6–3.8) will discuss some of the methods used over the last three decades to test glove materials and factors influencing glove use.

3.2 Polymers

3.2.1 General characteristics and definitions

Polymers are materials composed of macromolecular organic compounds that are formed by joining a large number of monomers (small molecules) in a chain. These macromolecules consist of arrangements of repeating monomer units to form linear chains, which in some cases are branched or connected to form three dimensional networks (Billmeyer 1971, p.4).

Homopolymers consist of a single repeating monomer and include both natural and synthetic polymers. Heteropolymers are composed of several repeating monomers, which include copolymers. Copolymers contain repeating units from more than one monomer. The main sub-classifications include alternating, random and block copolymers. Alternating copolymers are characterised by the attachment of one monomer to another in regular order, whereas random copolymers have monomers joined in a random fashion. Block copolymers have long sequences of the same repeating unit in a chain (Rudin 1982, pp.17–18; Seymour and Carraher 1981, p.320).

The *degree of polymerisation* (DP) is the length of the chain that is specified by the number of repeat units. The number of monomer units linked together varies and this phenomenon is responsible for the tensile strength, impact strength, molten flow characteristics and chemical resistance (Skinner 1992, p.8). Polymerisation refers to the chemical reaction where the product molecules are able to grow indefinitely in size while reactants are available (Rudin 1982, p.7).

Polymeric materials are employed in numerous applications including plastics, rubbers and elastomers. Polymers include anthropogenic plastics, and biological polymers such as rubber, wool and cellulose. Petroleum, coal and natural gas are starting materials for synthetic polymers being sources of ethylene, methane, alkenes and aromatics (Sawyer and Grubb 1987, p.1).

3.2.2 Classification of polymers

Commonly a tripartite nomenclature system is used—the International Union of Pure and Applied Chemistry (IUPAC), common or historical and industrial. The IUPAC system is the only formal system (Seymour and Carraher 1981, pp.xv–xvi). In this thesis classification will take a common perspective and focus on the end product or use rather than the manufacturing process (Stachurski 1987, pp.1–3). For example, polyvinyl chloride (PVC) is recognised in both the common and industrial classifications, but within the IUPAC system is Poly (1-chloroethylene).

Polymers can be divided into three major classes based on their thermal properties—thermoplastics, thermosets and rubbers or elastomers.

Thermoplastics are common polymers and customarily referred to as plastics. A thermoplastic is a polymer that when heated softens and flows, adopting a new shape on cooling. This process, of the thermoplastic softening upon heating and solidifying upon cooling, can be almost unlimited. They are composed of separate continuous chains with strong primary covalent bonds. The chains are held together with much weaker secondary bonds (Crawford 1985, p.9; Renwick 1990, p.28).

Thermosets may be shaped with the application of heat and pressure but the number of cycles is finite. Their structures are highly cross-linked with three dimensional networks formed by strong covalent bonds formed between the macromolecules. Characteristically they are rigid materials (Crawford 1985, p.10; Rudin 1982, pp.23–24; Stachurski 1987, p.9).

Elastomers, also known as synthetic rubbers, are amorphous polymers with a small number of cross-links. They exhibit rubbery-like qualities and can often be elongated up to $\leq 200\%$ with rapid retraction upon release (Engel *et al.* 1981, p.9; Hall 1981, p.52; Renwick 1990 p.19).

3.3 Polymer Morphology

Polymer morphology refers to the microstructure of the material above the atomic arrangement. Fillers and additives are also morphological features (Sawyer and Grubb 1987, p.3).

The next section covers some of the properties of crystalline and amorphous polymers plus their additives.

3.3.1 Crystalline and amorphous polymers

Solid polymers exist as crystalline or amorphous materials or in combination. Crystalline polymers are not entirely crystalline and have some amorphous regions (Stachurski 1987, p.14). These polymers are tough, have some flexibility and are not brittle. Flexion occurs in the amorphous regions. Increasing crystallinity has the effect of increasing strength, hardness, stiffness and density. Examples of crystalline thermoplastics include nylon and high density polyethylene (Renwick 1990, pp.28–31).

Amorphous polymers have jumbled chemical structures, due to large substituents, and therefore crystallisation is hindered. The dimensions of these substituents cause a reduction in segmental motion and slip due to stronger secondary inter-chain forces. They are generally glassy or rubbery at room temperature (Renwick 1990, p.32).

3.3.2 Additives

Nearly all polymers are oxidisable and many of them require stabilisation to resist the rigours of processing and environmental elements such as heat, oxygen and radiation. The appropriate use of polymers is maximised when additives are incorporated into the matrix in a process known as compounding (Crawford 1985, p.7). Additives are also used to enhance the optical, mechanical and surface properties of plastics.

A useful classification method is to divide them into two classes based on whether the modification is physical or chemical. Additives that are operational by physical means are plasticisers, lubricants, fillers and colourants. Those that modify the polymer by chemical means include ultraviolet stabilisers, antioxidants, antiozonants and flame retardants.

The important additives that are used in CPG manufacture are discussed in greater detail below.

3.3.2.1 Physical modifiers

3.3.2.1.1 *Plasticisers*

Plasticisers enhance the flexibility of polymers by reducing intermolecular forces. Lowering of melt viscosity, elastic modulus and glass transition temperature occur when plasticisers are added. Glass transition temperature (Tg) is the temperature at which free rotation of covalent bonds occurs that allows for segmental motion. Plastics need to be above Tg whereas elastomers need to be below. However longevity, stability and compatibility are the fundamental requirements for commercial polymer use (Billmeyer 1971, pp.500–501; Renwick 1990, p.70; Seymour and Carraher 1981, p.12).

Plasticiser action has been described by three theories—lubricity, gel and free volume. The lubricity theory expounds the notion that the polymer chains slip over each other as the plasticiser acts as an internal lubricant. The gel theory states that the plasticiser weakens the intermolecular attractions. The assumption in this theory is the existence of a pseudo three-dimensional structure. This theory is particularly relevant to PVC. Free volume refers to holes or spaces that are not occupied by polymer chains. It is assumed that plasticisers increase the free volume and that the free volume is identical for all polymers at Tg (Seymour and Carraher 1981, pp.376–378).

It is necessary for the plasticiser to have some degree of solvency within the host polymer and therefore solubility parameters should be matched. By way of illustration PVC is a hard rigid solid but with the addition of 50–100 parts by weight of phthalate ester plasticisers it converts to a leathery product suitable for upholstery and PPE. Plasticised PVC is amorphous and may contain up to 50% plasticiser. Solvents can modify the composition of PVC by inducing plasticiser loss (Renwick 1990, p.61). Rubbers are plasticised with petroleum products (Rudin 1982, pp.445–446).

Sometimes secondary plasticisers are used which may not be as compatible with the host polymer but are used for their synergistic effect (Rudin 1982, p.446; Seymour and Carraher 1981, p.390). That is, the secondary plasticiser may be inactive or only weakly active but will enhance the activity of the primary plasticiser.

3.3.2.1.2 *Lubricants*

Lubricants are used to improve production and for external aesthetics of polymers. Generally lubricants are not compatible with their host polymer. Lubricants can be sub-classified into two general areas of action, internal and external. In the first category there is a reduction in shear stress between individual resin molecules. In the

second category there is a reduction of shear stress at the macroscopic level. The external lubricants are much less compatible with the host polymer than the internal. Many lubricants can fulfil both roles.

External lubricants can be further sub-classified depending upon their functional purpose. Examples include release agents, slip agents, adherents, mould release agents, parting agents and anti-blocking agents (Radian Corporation 1987, p.99). Slip agents exude from the polymers and function as surface lubricants, which reduce the coefficient of friction (Rudin 1982, p.449).

Internal lubricants include the following chemical groups: fatty acids and alcohol; fatty acid amines; fatty acid esters; and metallic soaps. Stearic acid, which has a carbon chain length of 18, is the most common lubricant for PVC, where it acts as an external lubricant (Rosen 1971, p.256).

External lubricants include the following chemical groups: polyethylene waxes, paraffin and other waxes. Slightly oxidised polyethylene waxes are used in PVC pipe extrusion and in semirigid and flexible PVC (Radian Corporation 1987, pp.99–101).

3.3.2.1.3 *Fillers*

Fillers are inert substances that are added to increase bulk for cost efficiency. Fillers can improve hardness, impact, flexural and compressive strengths. Coupling agents frequently need to be used with fillers to ameliorate their bonding (Radian Corporation 1987, pp.66–75; Rosen 1971, pp.255–256).

3.3.2.1.4 *Colourants*

The purpose of colourants is to impart hue, value and chroma to plastics. Most colourants are added for aesthetic reasons, although some have other desirable qualities such as ultraviolet (UV) radiation stabilisation. Colourants include organic and inorganic pigments and dyes. Organic pigments are smaller in particle size, are brighter and less dense than the inorganic pigments. Dyes are only used infrequently in plasticised polymers as they migrate readily and are thermally and chemically unstable.

Pigments may be added in small amounts as solids producing opaque plastics or by the addition of liquid or solid organics that dissolve in a transparent polymer to give transparent materials. Salts and oxides of metals, such as titanium dioxide, iron oxides, cadmium, zinc, mercury, strontium and barium are classified as inorganic pigments. Carbon black, phthalocynines, mono and disazo compounds, indolines,

perylenes and quinacridones are organic pigments (Radian Corporation 1987, pp.44–55; Rosen 1971, p.256; Seymour and Carraher 1981, p.384).

3.3.2.2 Chemical Modifiers

3.3.2.2.1 *Antioxidants, antiozonants and ultraviolet stabilisers*

An antioxidant is a compound that retards oxidative degradation of the polymer within its life expectancy at ambient temperatures (Seymour and Carraher 1981, p.181). Antioxidants can be classified into primary and synergistic. Primary antioxidants arrest oxidation, which is a free radical chain process, by acting as free radical sinks or scavengers. The most widely used are phenols and the diaryl amines. The synergistic antioxidants destroy hydroperoxides, which are a source for free radicals.

Synthetic rubbers are highly unsaturated and their double bonds are extremely susceptible to oxygen and ozone attack. Antioxidants are important in synthetic rubbers particularly those that contain butadiene (Rosen 1971, p.263).

Ozone attack results in crack formation in synthetic and natural rubbers. There are two major types of antiozonant additives, microcrystalline waxes and *N,N*-dialkyl-*p*-phenylenediamines. The waxes are mainly used for static end-use conditions as their action involves diffusion to the surface where they form a film that is impervious to ozone but will not cope with flexion. In dynamic conditions waxes and/or *N,N*-dialkyl-*p*-phenylenediamines derivatives are beneficial (Loan and Winslow 1979, p.430).

Sunlight is the main source of UV radiation (280–400 nm) and can be destructive to polymers. For example PVC is degraded at 310 nm (Seymour and Carraher 1981, p.381). The C—C bond energy is approximately 330 kJ/mol, which is matched to a photon wavelength of 360 nm (Hall 1981, p.126). The energy of this radiation can cleave covalent bonds giving rise to free radicals that have the potential of chain scission, cross-linking and creating sites of unsaturation that affect the product by causing discolouration and embrittlement of organic polymers. Properties that are lost due to these processes are loss of tensile strength, loss of molecular weight and decrease in impact resistance and elongation prior to break (Radian Corporation 1987, p.128; Seymour and Carraher 1981, pp.381–382).

Absorption of UV radiation by polymers is primarily a surface phenomenon. Ultraviolet quenching and absorption are two important mechanisms specific to the reduction of the photo-initiation rate. Absorbers dissipate the absorbed energy by

converting it to heat or by emitting it as longer wave lengths as phosphorescence, fluorescence or infra red (IR) radiation. None of these phenomena are destructive to the polymer nor do they have any deleterious effects upon the stabiliser itself. Examples of absorbers are benzophenones and benzotriazoles.

Quenchers work by deactivating the free radicals, which were formed by the polymer in response to UV absorption and restore it to a non excited state before more reactions occur and the excess energy is emitted as harmless IR radiation. Organo-nickel compounds are examples of quenchers (Gugumus 1982, pp.17–20; Radian Corporation 1987, pp.128–132).

3.4 Polymer Degradation

Degradation of polymers refers to undesirable changes in properties while the material has been in use (Rodriguez 1982, p.277). Major processes of degradation include oxidation, photo-oxidation, hydrolysis, weathering, pyrolysis and radiolysis (Hall 1981, pp.120–121).

3.4.1 Weathering

Weathering gives rise to aging phenomena. Aging refers to processes that occur over time, weeks to years, at ordinary temperatures and normal atmospheric conditions. Natural weathering of polymers involves exposure to one or many factors such as wind-blown particles causing erosion, or radiation and chemical attack. During weathering the absorbed UV and absorbed IR radiations cause damage. Chemical attacks are mainly due to atmospheric oxygen and moisture. Thermoplastics can absorb water, which acts as a plasticiser (Crawford 1985, p.26; Engel *et al.* 1981, p.227; Vollmert 1973, p.125).

The rate of aging is inconstant and is conditional upon polymer type and prevailing conditions. Aging outcomes include the loss of mechanical properties, increasing brittleness and discolouration. Brittleness occurs at temperatures below Tg and is accompanied by increasing density. Discolouration is caused by the formation of conjugated systems of double bonds (Loan and Winslow 1979, p.425). The most serious effect of degradation is caused by UV radiation, which results in a loss of toughness, cracking and embrittlement. This deterioration is predominantly a process of oxidation. The rate of oxidation is dependant upon the thickness of the polymer and the climatic zone (Loan and Winslow 1979, p.125).

Generally, rubber materials have good weatherability but are subject to ozone attack. Most antioxidants will only act as a safeguard for one to two years, during which time

there will be a gradual deterioration due to oxidation and volatilisation (Bartenev and Zuyev 1968, p.404). Sunlight can cause surface cracking although this is only superficial. Oxygen causes degradation through chemical breakdown.

3.5 Mechanical Failures Of Polymers

Historically, the failure of polymers has been explained as a process of break under the effect of stress and thermal oscillation of chains in the whole mass of material. The strength of polymers is attributed to their plastic flow behaviour, or toughness. Most scientific endeavours that examine solid polymer failures involve investigations of crack or craze propagation (Bartenev and Zuyev 1968, p.104; Matsuoka and Kwei 1979, p.392).

Crazing and cracking are two important phenomena that warrant more detailed attention. These types of failures are mainly associated with amorphous polymers. In the presence of low molecular weight liquids these manifestations will occur at considerably lower stress levels. Chemical degradation, plasticisation and internal stresses created from penetrant molecules, either singly or in combination, form part of the mechanisms behind craze and crack formations (Marom 1985, p.371). These types of failures are discussed in the following sections.

3.5.1 Crazing

Crazing is the formation of thin sheets that are perpendicular to the tensile stress direction that contains fibrils and voids, which may extend through, on/or under a polymer surface (DuBois and John 1974, p.396). Fibrils and voids are aligned parallel to the tensile strength direction. These fibrils have diameters between 0.01–0.1 mm.

Crazing refers to localised fine cracking. It is not classified as polymer failure but rather as a normal response to continuous slow tensile stress to relieve loaded parts of the material (Engel *et al.* 1981, p.140). Craze formation involves the absorption of energy and provides areas of low density. Crazing can be caused by organic liquids and gases and can be a precursor to cracking. For example, when crazing occurs on the surface, an attacking agent will have easier penetration (Billmeyer 1971, p.234; Williams 1989, p.260). It is included in this section because it can be a precursor for other types of failures in polymers.

Crazes scatter light and can be seen by the naked eye as whitened areas and are sometimes regarded as blemishes. However, crazed material does maintain its original strength (Hall 1981, p.120).

3.5.2 Cracking

A crack is essentially a brittle failure and it is characterised by the formation of new surfaces. Cracking can be local or may effect the whole material (Bartenev and Zuyev 1968, p.23). Surface energy is the energy of the laid open area minus the energy of the closed surface. The creation of a crack involves the surface energy plus the dissipated energy that occurs during propagation of the crack (Matsuoka and Kwei 1979, p.392). Within the technical literature there is a plethora of descriptions of crack types and causative agents, some of which are discussed next.

3.5.2.1 Environmental stress cracking

Environmental stress cracking (ESC) is when the specimen fails in liquid or aqueous media while exposed to mechanical stresses (Billmeyer 1971, p.133). Environmental stress cracking occurs when a specific attacking medium and tensile stress are simultaneously applied to a delicate material. This type of failure mainly effects amorphous polymers. There are a number of theories that have been put forward to explain the mechanism of ESC. A contemporary explanation is that environmental agents penetrate and plasticise the polymers thus reducing the critical level of strain at which the crack will form (Crawford 1985, p.26; Engel *et al.* 1981, p.277; Hall 1981, p.120).

3.5.2.2 Ozone cracking

Synthetic and natural rubbers (NR) are subject to atmospheric ozone attack, and characteristically they develop ozone cracking when under stress. These cracks are perpendicular to the direction of tension and are a surface feature. The O_3 molecule attacks the C=C bond, which leads to scission in the main primary chain (Hall 1981, p.123).

3.5.2.3 Embrittlement

Brittleness refers to the property of solids where they separate into pieces without going through a plastic stage. Embrittlement is caused by chain scission reactions (Loan and Winslow 1979, pp.425–427). Brittle fractures do not cause any noticeable deformation related to viscous flow. These fractures spread transversely through the material. Applied tensile stress gives rise to tearing whereas compression stress gives rise to shearing (Bartenev and Zuyev 1968, p.42; Engel *et al.* 1981, p.177).

The occurrence of brittle fractures is more pronounced in polymers with low molecular weight, stiff chains and is intensified with low temperatures and increasing stress application. In brittle fractures there is very little absorption of energy, although there

is primary bond breakage when the polymer T<Tg in the amorphous regions (Rudin 1982, pp.379–390; Williams 1989, pp.257–259).

Engel *et al.* (1981, p.177) defined brittle fractures as "deformation with fibrils about 1 mm long or less". The fractures were described as fracture surfaces that were covered by thin (<1 mm) layer, which had been stretched and damaged so that the surface resembled "lifted oval lids", "stepped" and "striped" patterns. This damaged surface then allows one to assess the direction of fracture propagation. Polymer specimens that have had a brittle fracture remain essentially the same apart from the fracture.

3.5.2.4 Ductile fractures

During ductile behaviour the polymer chains will realign in the direction of the applied stress. There is secondary bond breakage accompanied by chain slippage and this allows for a great deal of energy absorption and a high degree of toughness. Ductile behaviour is associated with T >Tg, low strain rates, mobile chains and high molecular weight. Generally the specimen will exhibit necking or thinning prior to fracture (Williams 1989, pp.257–258). Following the fracture the specimen surface will be deformed, *e.g.* the surface may show ramps, folds and waves. Chemical attack results in a reduction of intermolecular bonds, which will increase ductility.

Engel *et al.* (1981, p.152) have made a discretionary division in ductile fractures based upon the length of the fibrils remaining in the fracture zone.

> Polymers with high plastic deformation up to the fracture-length of remaining fibrils >10 mm.
> Polymers with low plastic deformation up to the fracture-length of remaining fibrils >1-10 mm.

Polyvinyl chloride will withstand a high degree of plastic deformation.

3.5.2.5 Imperfections and crack propagation

Faults in polymeric materials have a significant impact upon their performance. Faults are typically surface features and include such things as cavities, inclusions and heterogeneities.

Cracking can also be attributed to polymer imperfections. In plastics the frequency of surface cracking is much greater than internal cracking (Bartenev and Zuyev 1968, p.98). Several theories of crack propagation have been developed and most have their genesis from the Griffith Theory of Flaws. This theory, published in 1920, related to glass but since then has been applied to many materials (Treloar 1970, p.139). The theorem suggests that the discrepancy between hypothetical and observed strength is

due to flaws in the material. This can be expressed algebraically as (Matsuoka and Kwei 1979, pp.394-395):

$$(\partial U/\partial C) + (\partial \Gamma/\partial C) < 1$$

where U is the recoverable strain energy, Γ is the energy required to create the crack surfaces and C is the crack surface.

So only when the applied stress exceeds the critical value will the crack propagate. The stress is concentrated at the tip of the crack where progressive failure occurs and the finer the crack the greater the magnification of the stress.

A cavity is a general term that covers concave forms such as holes, bubbles, pores and sink marks. Cavities are generally smooth as they have been formed by free forces, as opposed to mechanical and fracture damage (Engel *et al.* 1981, p.41).

3.5.2.6 Pseudo-cracking

Pseudo-cracks are wedge shaped regions that can give rise to deformation and partial delamination that may be a precursor to failure (Bartenev and Zuyev 1968, p.100). This type of cracking is often in response to minor but constant tensile stress. It is determined by the relationship between the speed of the low elastic deformation in the overstressed places of the material and the speed of the propagation of the failure cracks.

Pseudo-cracking is not necessarily a permanent feature. For example, pseudo-cracking may be generated from a fault in a stressed polymer surface and altering the conditions, such as removal of the stress or annealing the polymer, may result in a restorative action (Bartenev and Zuyev 1968, pp.101–102).

3.6 Gloves

There are nine commonly used polymers that are used in CPG manufacture (Table 3.1) (Forsberg and Faniadis 1986; Perkins 1987; Watterson 1988, p.59).

TABLE 3.1

Common polymers for chemically protective gloves

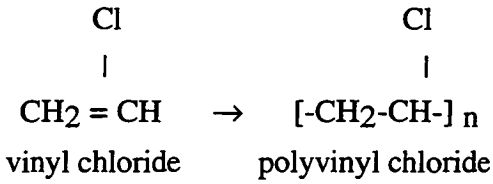
Polymer	Components	Description
Butyl rubber	97% isobutylene/3% isoprene copolymer	Synthetic rubber. Good chemical resistance properties. Impermeable to gases.
Natural rubber	Isoprene	A distilled product from the gutta percha trees. If untreated has little chemical resistance.
Neoprene	Chloroprene	Trade name from Du Pont Company for a rubber like product. Oil, oxygen and heat resistant.
Nitrile rubber	Random or alternating acrylonitrile/ butadiene copolymer	Synthetic rubber. Oil resistant.
Polyethylene	Ethylene	Plastic material; often used as a coating.
Polyvinyl alcohol	Vinyl alcohol	Plastic that has some solubility in water but very good resistance to organic solvents.
Polyvinyl chloride	Vinyl chloride	Plastic material. Oil and water resistant.
Urethane	Polyisocyanate and polyol	Resistant to solvents and good weatherability.
Viton	Hexafluoropropylene/vinylidene fluoride copolymer	Rubber like copolymer. Oil resistant.

Chemically protective gloves for farm pesticide use are typically made from especially manufactured PVC or nitrile rubbers and therefore these materials are explored in more detail below.

3.6.1 Polyvinyl chloride

Polyvinyl chloride is a colourless solid with outstanding resistance to water, alcohols and concentrated alkalis and acids. Compounded with plasticisers it produces a flexible material that is superior to rubber in its aging properties.

Polyvinyl chloride is a thermoplastic. It is primarily atactic but partially syndiotactic. That is to say that the Cl atoms are placed randomly on either side of the chain (Stachurski 1987, p.102). The gaseous vinyl chloride monomer (VCM) is generally made by the oxychlorination of ethylene to ethylene dichloride (EDC). Vinyl chloride is manufactured by thermally cracking EDC (Skinner 1992, p.42). A free radical mechanism is activated by catalyst action that achieves polymerisation. The VCM has two sites, the alkene carbon atoms, at which reaction takes place. The double bonds between the carbon atoms are opened by the catalyst and thus the VCM units link to form long chains, which are branched rather than linear (Billmeyer 1971, p.419; Renwick 1990, p.25; Skinner 1992, p.42).



Polyvinyl chloride is moderately unstable to heat and light. The stability of the C—Cl bond is reduced with thermal initiation. The chlorine radical separates a hydrogen bond to give a HCl. The resulting chain radical then reacts to form chain unsaturation with regeneration of a chlorine radical. Ultraviolet light can also initiate this reaction by being absorbed at unsaturated structures with liberation of an adjacent chlorine atom. Oxygen accelerates both chain reactions and ketonic structures are formed in the chain (Billmeyer 1971, pp. 419–420).

3.6.2 Acrylonitrile-butadiene rubber

Synthetic rubbers are manufactured from oil based products such as butadiene, styrene and acrylonitrile. They have long chain structures and thus imitate natural polymers. The nitriles are organic compounds containing the cyanide group. Nitrile rubber (NBR) is a copolymer of acrylonitrile, 20–50%, with butadiene (Hibbert and James 1987) p.320. This copolymerisation is usually achieved by free radical emulsion and is typically cross linked with sulfur (Burford 1989, p.205; Crawford 1985, p.68). Monomer, water, surfactant or emulsifier or dispersant and a catalyst are the basic constituents necessary for emulsion polymerisation, (Table 3.2) (Renaud 1993).

TABLE 3.2

Typical components used in the polymerisation of nitriles suitable for chemically protective gloves

Monomer solution	Aqueous solution	Redox initiator	Final stage
Acrylonitrile	Demineralised water	Sodium sulphoxylate	Ammonia
Butadiene	Sodium alkyl aryl sulphonate	Cumene hydroperoxide	Antioxidants
Acrylic acid	Polynaphthalene sulphonate	Ferrous sulphate	Biocidal agents
Alkyl mercaptan	Electrolytes	EDTA salt	

The formula for NBR is:

$$-CH_2CH = CHCH_2CH_2CH(CN)-$$

The outstanding characteristic of NBR is its solvent resistance, by which it is tacitly implied that it has low solubility, low swelling, good tensile strength and abrasion resistance following immersion in oil. Increasing the acrylonitrile content also increases the degree of oil resistance, because the elastomer becomes more polar, but simultaneously low temperature flexibility is sacrificed. This solvent resistance is associated with high solubility parameters of polar nitrile groups, which is directly related to the monomer ratios. A typical monomer solution for nitrile rubbers includes acrylonitrile, butadiene, acrylic acid and alkyl mercaptan. Anionic emulsifiers, such as those from the sulphonate or alkylether sulphate groups are essential for polymerisation in an acid medium. At the final stage of polymerisation the pH is adjusted to a value of approximately 8.0. This is achieved by the addition of ammonia or potassium hydroxide and results in improved mechanical stability (Renaud 1993).

The inferior characteristics of NBR are related to moderate mechanical properties and therefore fillers and additives are required. It also has a very low working temperature range (Billmeyer 1971, p.396; Burford 1989, p.205; Rodriguez 1982, p.397).

3.6.3 Manufacturing processes

Essentially there are three main manufacturing procedures for processing CPC, which are solvent dipping, latex and milling. The first two are used for glove manufacture and the latter for larger clothing items. For dipping a hand form is submerged in the polymer solvent solution. The unit is transferred to the air where the solvent volatilises and the polymer hardens on the form. In the latex process the hand form is dipped into an aqueous polymer emulsion. Nitrile rubbers are especially formulated for the dipping process (Engle and Nusbaum 1984; Ness 1994, pp.46–47; Perkins 1987; Schwartz and Dougherty 1987).

3.6.4 Standards and methods for testing gloves

Prior to the 1970s there were very little published data on the efficacy of CPGs. From the early 1970s glove manufacturers began to issue guides based upon degradation characteristics (Leinster *et al.* 1990). The rationale for the ratings stemmed from alterations of the physical properties such as elongation, tear resistance and abrasion (Williams 1979). Interest in glove protective qualities heightened in the late 1970s, which accompanied the growing concern over chemical use and cancer studies, and the interest in hazardous waste management. A perspicacious study from the 1970s determined that the thickness of the glove was not the main contributing factor to chemical protection but placed more emphasis upon the glove's material composition (Weeks and Dean 1977). Subsequently, the glove selection guides provided crude descriptions of how a particular glove would endure immersion in liquid chemicals. The gloves were then reported as poor, good and excellent for a particular chemical (Perkins 1987). During the 1980s the focus of glove permeation studies was on neat solvents. There were very few studies that examined permeation of higher molecular weight compounds such as are present in multicomponent compounds and the active ingredients of pesticides (Schwope *et al.* 1992). Little attention was given to the needs of the agricultural worker (Watterson 1988, p.59).

Factors that influence glove integrity include manufacturing processes, temperature, thickness, use and the pesticide and/or solvent glove interaction (Schwope *et al.* 1992). A variety of testing methods has been developed to incorporate and to allow for these factors. There are several current guides for glove selection (Ansell Edmont 1990; Ansell Edmont 1991; Forsberg and Mansdorf 1993). However, the recommendations are usually made from permeation data related to their resistance to pure compounds on unused gloves in laboratory conditions (Bromwich and Smith 1995; Ehntholt *et al.* 1989).

Contemporary methods and standards for testing glove efficacies were developed by the Committee F-23 Protective Clothing for the American Society for Testing and Materials (ASTM). This committee now has several dedicated sub-committees, which explore avenues related to protective clothing, physical hazards, chemical resistance and clothing classification (Berardinelli and Linn 1989). Initially these tests were designed to measure material changes to CPGs after contact with hazardous liquid chemicals (Mickelsen *et al.* 1986). The British Occupational Hygiene Society Technology Committee Working Party has a similar working history (Leinster *et al.* 1990). The British Standards for protective gloves have the same status as the European Standards. The British Standards Committee is in process of developing a test method for degradation. In Australia the current standard is outdated and draft standards are in place awaiting ratification; these drafts are the same as the British ones, with no degradation test methods in place.

The relevant international standards for glove testing are listed in Table 3.3. Standards in text will now be referred to by their identity codes.

TABLE 3.3

Current chemically protective glove standards

AS2161 Australian Standard Industrial Safety Gloves and Mittens. Standards Australia, 1978.

ASTM F739:1991 Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases. American Society for Testing and Materials 1985.

ASTM F903: 1996 Standard Test Method for Resistance of Protective Clothing Materials to Penetration by Liquids. American Society for Testing and Materials 1984.

BS EN 374-1 1994 Protective Gloves Against Chemicals and Micro-organisms. Part 1. Terminology and Performance Requirements. British Standards.

BS EN 374-2 1994 Protective Gloves Against Chemicals and Micro-organisms. Part 2. Determination of Resistance to Penetration. British Standards.

BS EN 374-3 1994 Protective Gloves Against Chemicals and Micro-organisms. Part 3. Determination of Resistance to Permeation by Chemicals. British Standards.

DR 95446 Draft Australian/ New Zealand Standard for Comment "Industrial Gloves and Mittens". Standards Australia, June 1993

DR 95462 Methods for Evaluating Gloves and Mittens Against Chemicals and Microorganisms. Part 1. Terminology and Performance Requirements. Standards Australia.

DR 95463 Methods for Evaluating Gloves and Mittens Against Chemicals and Microorganisms. Part 2. Determination of Resistance to Penetration. Standards Australia.

DR 95464 Methods for Evaluating Gloves and Mittens Against Chemicals and Microorganisms. Part 3. Determination of Resistance to Permeation. Standards Australia.

ISO 6529: 1990 Protective Clothing-Protection Against Liquid Chemicals. Determination of Resistance to Air Impermeable Materials to Permeation by Liquid Chemicals. International Organization for Standardization.

3.7 Chemical Transmission Through Glove Materials

Permeation and penetration are the two modes of transmission of chemicals through gloves. Permeation studies dominate the glove literature encompassing a great diversity of methods and procedures. The variety of studies and different analyses are discussed in the following sections. This diversity makes comparisons extremely difficult. Penetration and permeation mechanisms are not mutually exclusive, but they will be examined separately in the next sections, followed by some problematical generalities related to permeation theory. Traditional permeation theory and its application to gloves are discussed first.

3.7.1 Permeation theory

Permeation is the movement of a chemical through the glove material at the molecular level (Forsberg and Mansdorf 1993, p.96). This movement involves absorption, diffusion and desorption.

Polymeric materials are composed of crystalline and amorphous regions and it is the thermal motions occurring in the amorphous regions that allow the permeating molecules through (Perry and Green 1984, pp.17–14). Plasticisers, particularly dioctyl phthalate, may also enhance permeability of solutes because they allow for the polymer chains to move easily and interchange with penetrant molecules (Jenke 1993; Vahdat and Delaney 1989). The fundamental premise underpinning permeation testing is Fickian Diffusion. Fick's law is a mathematical expression of diffusion of liquids and solids. Fick's first law can only be applied to diffusion in the steady state, that is when the concentration gradient does not vary with time and is expressed by the equation:

$$F\chi = -D(\partial c/\partial \chi) \qquad (1)$$

where F is the flux and D is the diffusion coefficient. D is independent of the penetrant concentration. The flux is proportional to the concentration gradient (Windle 1985, pp.77–78).

Fick's second law of diffusion applies to the non steady state and has several applied formulae which are sagaciously described by Crank (1975). A modification of Fick's second law of diffusion when the diffusion is limited to the x direction is illustrated in equation 2 (Comyn 1985, p.3).

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial \chi^2} \qquad (2)$$

The British Standard *(BS EN 374-3:1994)* defines the permeation rate, for closed loop systems as illustrated in equation 3:

$$\frac{\text{concentration of the challenge chemical} \times \text{flow rate of the collecting medium}}{\text{sample surface contact area}}$$

$$P = \frac{\left(C_i - C_i - 1\right) V_t}{\left(T_i - T_i - 1\right) A} \qquad (3)$$

where P is the permeation rate; $\mu g/cm^2/min$. A is the sample area in contact, i is the index number assigned to each discrete sample commencing with $i = 1$. T_i is the time i is removed recorded in minutes. C_i is the chemical concentration detected in the collecting medium measured in $\mu g/L$ at T_i. V_t is the complete collecting medium, expressed in litres.

Permeation testing encompasses two notable indices. The first is breakthrough time (BT) and the second is steady state permeation rate (SSPR). Breakthrough refers to "the movement of a chemical through to the other side" (Forsberg and Mansdorf 1993, p.92). Breakthrough time is the time taken for the chemical to emerge from the external surface to the internal surface (Forsberg and Mansdorf 1993, p.92). The rate of permeation increases until it reaches the SSPR, in other words the concentration does not increase with time. The SSPR is lower in organic solids than liquids probably due to the lower vapour pressure (Fricker and Hardy 1992).

Reliance upon BT is enigmatic as it is highly dependant upon analytical sensitivity and it is difficult to make comparisons between experiments (Perkins and Knight 1989). Breakthrough time also pivots upon procedural differences, *e.g.* the surface area of the sample and the flow rate of the collecting medium (Schwope *et al.* 1988). Likewise the diffusion coefficient cannot serve as a sole practical indicator because it can only be determined following SSPR, that is exposure has already occurred (Silkowski *et al.* 1984). Dependence upon BT is also problematical when the challenging agent is a complex mixture, *e.g.* a pesticide formulation, as the different constituents may permeate at different rates and change the permeation profile of the constituent that is being analysed and this is further compounded if only one constituent is being analysed (Davis *et al.* 1986). The sample position on the glove is an important factor influencing BT. Bromwich *et al.* (1994–1995, pp.74–75) reported a greater variation

of BT over the surface of PVC gloves than between gloves from the same batches. All these problems have given rise to a misapplication of permeation data (Stull and White 1992).

3.7.2 Permeation testing

Assessment of polymer permeability involves the measurement of the rate of transfer of the permeant through the sample thickness per unit area and pressure difference (Billmeyer 1971, p.133). Permeation testing is typically conducted in controlled laboratory conditions using a permeation cell, which is divided into two compartments by the clamped glove material specimen. The hazardous chemical is contained by the exterior surface of the specimen and the collecting medium on the interior surface. The collecting media are either liquids, such as water, or gaseous such as dry air, nitrogen or helium that do not affect the polymer (Schwope *et al.* 1988). Open and closed loop systems are frequently used with either continuous or discrete sampling methods. With open loop systems the fresh collecting medium is passed through the receiving chamber at a constant flow rate. In closed loop systems the medium is trapped within the receiving chamber and this enables a total permeation rate to be detected. Of course there are many variations and combinations of these techniques (Schwope *et al.* 1988). Early glove permeation test cells were unsophisticated although the basic principles are still in use today.

Analytical techniques recommended by the *BS EN 374-3 1994* include liquid and gas chromatography, colorimetry, UV and IR spectroscopy and radionuclide tagging detection counting. The minimal analytical sensitivity for the test chemical is $1\mu g/cm^2/min$ from the exposed specimen.

The standard for *Protective Gloves Against Chemicals BS EN 374-3* (1994) allows for other permeation cells to be used on the proviso that the standard permeation cell is used as the reference cell with emphasis on precision and bias in BT. Consequently there have been many comparative technical papers related to cell designs, some of which are discussed next (Berardinelli *et al.* 1983; Bromwich 1992; Henry and Schlatter 1981; Mellstrom 1991a; Mellstrom 1991b; Mellstrom *et al.* 1991; Moody and Nadeau 1993; Moody and Ritter 1993; Nelson *et al.* 1981).

3.7.2.1 Permeation cell comparisons

There have been several comparative investigations of different or modified test cells and procedures (Berardinelli and Moyer 1988; Ehntholt *et al.* 1990). Mellstrom (1991a; Mellstrom 1991b) demonstrated that significant differences in BT are system dependent as opposed to differences between two test cells. A comparison of an

automated *in vitro* diffusion analysis (AIDA) to the *ASTM F739-85* indicated that there was consistency between the two methods but acknowledged that the former method was more precise, and due to the automatic factor was probably less likely to incur operator error and the speed of the procedure was more likely to imitate field conditions as there would be less likelihood of pesticide deterioration (Moody and Ritter 1990).

A comparative study exploring the *ASTM F739-85* permeation cell and the Draft International Standard *ISO/DID 6529 (1988)* found that in spite of their differences the results were basically comparable (Mellstrom 1991a). A novel study using a modified *ASTM-85* test cell to cater for organic solids with an open loop system found that organic solids did indeed permeate gloves (Fricker and Hardy 1992).

Bromwich *et al.* (1994–1995, pp.44–45) developed the "Griffith Small Cell" to complement an HNU photo-ionisation detector and the "Bromwich/Smith Intermittent Cell". The small cell allows for biopsies from the same glove to be taken from different locations. The intermittent cell allows for discontinuous wetting and drying of the sample to simulate real work exposures to solvents.

Some researchers have found the reference cell too cumbersome and too costly for common use in industry and education and have produced simplified cells to suit specific needs (Bromwich 1992). Others have found it too fragile and replaced the glass sections with stainless steel (Davis *et al.* 1986, p.9).

The thickness of the glove materials and the temperatures that they are exposed to in permeation testing are extremely important considerations and are discussed in the next two sections.

3.7.2.2 Thickness

Glove thickness is a pivotal point influencing permeation test results. By the very nature of the manufacturing process glove thickness is not uniform. The finger tips are the thickest points and the interstices between the fingers the thinnest (Berardinelli and Hall 1985). Nelson *et al.* (1981) reported that glove permeation was inversely proportional to glove thickness. These researchers noted that this observation was not consistent when the same material came from different sources.

Many papers record specimen thickness and weight from a 5 cm sample, which in accordance with the *ASTM F739-85* (1986) cell, is taken from the cuff or palm of the glove. Bromwich and Smith (1995) noted significant differences in permeation and

thickness from different areas of PVC gloves. It is inherently difficult to measure glove thickness accurately with a micrometer, especially in lined or bonded gloves.

The thickness of the sample also has a major impact upon BT. Generally the BT increases with increasing sample thickness. In an unusual permeation study the glove thickness was determined in the manufacturing process by controlling the dipping and drying times; the gloves were subjected to a variety of chemical challenges using a modified ASTM method. The reported results stated that BT was increased with increased glove thickness and that BT was more likely to be influenced by different thickness rather than permeation rate (Schlatter and Miller 1986). There is some disparity within the literature concerning the exact role of thickness within a statistical framework. Some researchers support the concept that BT is directly proportional to glove thickness (Berardinelli and Hall 1985; Jencen and Hardy 1989; Sansone and Jonas 1981a). Schwope *et al.* (1988) disagree with this concept when an open loop system is used as although BT increases with increasing thickness it is non-linear. A puzzling result was obtained in a study comparing unsupported and unlined nitrile gloves with supported and lined nitrile gloves and supported unlined gloves, for 2,4-D isooctyl ester permeation rates; these tests found that the thinner unsupported and unlined gloves were superior in their permeation resistance properties (Harville and Que Hee 1989). It should be noted that these authors do not provide definitions of the terms "lined" and "supported" and it can be assumed that the lined gloves were not bonded to the glove material.

A method of normalising BT to exclude statistical differences based upon the thickness parameter was advanced by Sansone and Jonas (1981a). This method has been adopted by several researchers (Berardinelli and Hall 1985; Silkowski *et al.* 1984). It is based upon the above concept, which can be further elaborated as a linear dependence upon the square root of time. A statistical summary follows.
It should be noted that in the original work by Sansone and Jonas (1981a) thickness is represented as L. However, in this thesis it is converted to lower case in order not to be confused with lag time:

$$t^{1/2} = a + bl \qquad (4)$$

where a and b are representing constants in the permeation test system and l is the thickness.

When 0.1% of the permeant, by weight, has been measured then equation 5 can progress to equation 6:

$$t^{1/2} b \left(l - l_c\right) \qquad (5)$$

$$l_c \equiv -a/b \qquad (6)$$

where l_C is the critical thickness, that is, where permeation of 0.1% of the permeant is instantaneous. When time is predictable the fraction of l_C can be calculated, using equation 5, by setting $t^{1/2}$ to 0. The l_C/l ranges from 0–1 and the closer l_C/l is to unity the greater the risk of failure due to minor variations in thickness (Sansone and Jonas 1981a).

Thickness is frequently not a constant factor for the duration of many types of permeation tests, which is an assumption using Fickian Diffusion equations. For example swelling of the specimen from solvent exposure will alter permeation profiles (Nelson *et al.* 1981; Zellers *et al.* 1992; Zellers and Zhang 1993).

3.7.2.3 Temperature effect

Temperature is an extremely influential factor upon BT and SSPR. Increasing temperature reduces BT and increases SSPR (Perkins 1987; Jencen and Hardy 1988; Vahdat 1987). This is only partially supported by Zellers and Sulewski (1992) as illustrated in equation 7. They observed a decrease in BT and an increase in SSPR when the temperature was increased from 25° C to 37°C. These researchers examined several types of gloves using a standard reference cell *(ASTM F739-85)* for permeation of propylene glycol monomethyl ether acetate, which is a solvent used in semi-conducting industries. Butyl gloves were most resistant to this test procedure and the increasing temperature had no effect on the permeation profile.

$$P = P_o \exp(-E_p/RT) \qquad (7)$$

where P is the permeability coefficient, P_o is the pre exponential factor, E_p is the activation energy, R is the universal gas constant and T is the Kelvin temperature (Zellers and Sulewski 1993).

During pesticide application procedures there is a temperature gradient formed between the external glove surface, the contaminating agent and the skin. These are substantive temperatures that are crucial, rather than ambient temperatures, in farming situations.

Decontamination procedures involving used gloves exposed to high temperatures have revealed some possibilities for glove re-use in industry. Air drying at ambient temperatures was not inadequate for butyl gloves exposed to ethylene glycol dimethyl ether, but when exposed to 50°C there was a significant increase in BT without causing degradation (Menke and Chelton 1988). Butyl rubber and Teflon® were selected from a series of eleven glove materials tested for their resistance to four organic solvents to simulate gloves in re-use. This involved air drying the samples for twenty-four hours and then retesting with the permeation test cell. Butyl rubber exhibited a dramatically shorter BT and a low permeation rate whereas Teflon® was more or less unchanged (Stampfer *et al.* 1984). Teflon® (tetrafluoroethylene) has excellent thermal and chemical resistance properties but poor physical characteristics. Regardless of that, it is often incorporated into protective clothing and is manufactured by DuPont (Forsberg and Mansdorf 1993, p.98).

Several theoretical models have been developed to determine glove permeability and are examined in the following sections.

3.7.2.4 Film permeation lag time method

Lag time is an extrapolation from the SSPR curve, and an elaboration of this concept follows.

Experimentally a gas will permeate from a higher to a lower pressure through a film thickness. Generally the thickness *l* divides two cells containing permeable gas or vapour. It is assumed that the system is initially free of permeant and then gas pressure p1 is introduced into chamber one. This can be expressed as:

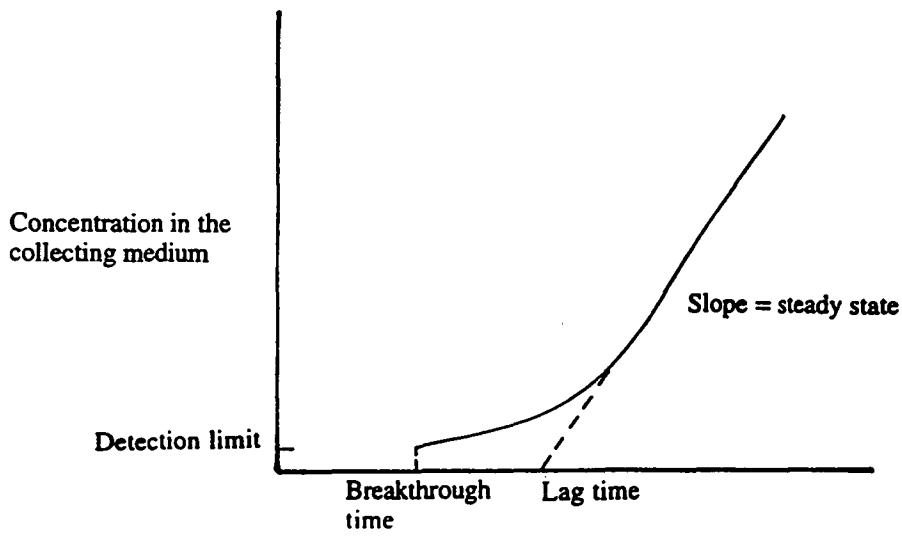
$$\frac{Q}{lC_1} = \frac{Dt}{l^2}\frac{1}{6}\frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left(-Dn^2\pi^2 t/l^2\right) \qquad (8)$$

where Q is the diffusing chemical, l is the thickness and C_1 is the concentration gradient in chamber 1 neighbouring the external surface of the glove sample.

At the interface it is assumed that a state of equilibrium is reached immediately followed by a linear buildup to steady state, that is when time is infinite. The lag time is derived from an intercept of the time axis from the SSPR curve (Comyn 1985, pp.1–8; Crank 1975, pp.49–53), (Figure 3.1).

FIGURE 3.1

Illustration of lag time according to a Fickian Diffusion model showing the extrapolation of the SSPR to the time axis in a closed loop system



This method is often used for calculating diffusion of gases in polymers (Moisan 1985, p.130), and for percutaneous absorption studies (Kubota *et al.* 1993; Oestmann *et al.* 1993), and is represented by equation 9.

$$Qt = \frac{DC_1}{l}\left(t - \frac{l^2}{6D}\right) \qquad (9)$$

This can then be intercepted on the t axis. The intercept point is represented by L which is the lag time, as seen in equation 10 (Crank 1975, p.51).

$$L = l^2/6D \qquad (10)$$

The advantage of using L as a permeation indicator over using BT exclusively is that it is not reliant upon analytical sensitivity (Que Hee 1996). However, the encumbrance of this technique is its reliance upon SSPR. It is often difficult to determine when a state of SSPR is reached, *e.g.* it may be misinterpreted for the plateau region (Figure 3.2) and this is a time problem (Perkins 1987). There is room for a big margin of error using this method as a major problem entails measuring the glove thickness accurately, which is often not static during the experiment.

Brooks and Bromwich (1993) nominated lag time and SSPR as a combined performance indicator for gloves and reported that a decrease in lag time is accompanied by an increase in permeation. This is obvious given that the lag time is an extrapolation from the SSPR curve, and therefore the steeper the curve the shorter the lag time. These researchers challenged NBR gloves samples with toluene using an in-house designed test cell with repeat tests done on five occasions over a nine day period. Unfortunately neither ambient conditions nor sample thickness were recorded, and therefore repeatability for other researchers is not possible. This method is perhaps too simplistic to warrant further consideration.

3.7.2.5 Solubility parameters

Solvation refers to the swelling of polymer molecules and it is the first stage that occurs when polymers dissolve. This primary swelling is related to the cohesive energy density (CED), which is the molar energy per unit volume and is equal to the strength of intermolecular forces. Following solvation the swollen particles disintegrate and/or disperse (Seymour and Carraher 1981, pp.61–66).

A solubility parameter is defined as a numerical value equivalent to the square root of the CED (Seymour and Carraher 1981, p.79). Solubility parameters are described as a measure of the strength of intermolecular cohesion in the pure solvent or in the pure polymer. The solvent solubility parameter is calculated from the energy of vaporisation. For the polymer, it is obtained indirectly and is estimated from the primary structure of the chain. The significance of the solubility parameter is that polymers are only soluble in solvents of similar solubility parameters (Hall 1981, p.115). The polarity of most solvents decreases as the molecular weight increases, but this is not the case for hydrocarbons. Three-dimensional models have been developed to accommodate hydrocarbons into solubility parameters. The parameters include the dispersion parameter, the hydrogen bonding parameter and the polar parameter (Perkins *et al.* 1986). The dispersion parameter is initiated when a non-polar molecule fluctuates and this is related to its transient dipole periods. This happens because there is a slight polar charge on the molecule, which is dependent upon the negative charge originating from an electron cloud and consequently influences its position. The dispersion parameter is solely associated with the solubility parameter of saturated non-polar hydrocarbons. The hydrogen bonding parameter refers to hydrogen protons joined by non-covalent bonds to unshared electrons of another molecule, and can be associated with polar compounds, for instance water. The polar parameter is associated with exposed oxygen, fluorine and nitrogen and is related to permanent dipoles of polar molecules (Perkins and Tippit 1985). Several theories have been developed encompassing these solubility theories.

Zellers (1993) developed a solubility model based upon the weighted difference between the solvent and polymer three-dimensional solubility parameters as illustrated in equation 11. Different weighting factors need to be used based upon the chemical class of the solvent and generally this involves weighting the hydrogen and polar parameters but not the dispersion parameter.

$$A_w = \delta_1 - \delta_2 = \left[a\left(\delta_{d1} - \delta_{d2}\right)^2 + b\left(\delta_{p1} - \delta_{p2}\right)^2 + b\left(\delta_{h1} - \delta_{h2}\right)^2 \right]^{1/2} \quad (11)$$

where δ_1 is the solvent solubility parameter and δ_2 the polymer solubility parameter. The subscripts are; *d* represents the dispersion parameter, *p* the polar parameter and *h* the hydrogen bonding parameter. a and b represent the weighting factors from the solvent chemical classes. Solubility and permeation should decrease as A increases (Perkins *et al.* 1986).

Solubility parameters will decrease with increasing temperature. Arrhenius relationships were used to plot solubility and permeation data versus increasing temperature in a study exploring N-methylpyrrolidone permeation through NR and butyl gloves. The results from this study indicated that increasing permeation associated with increasing temperature is related to the diffusion coefficient of N-methylpyrrolidone rather than the equilibrium solubility. This particular model was not as accurate as other models described in this study that were based on Fickian Diffusion in conjunction with equilibrium solvent solubility and the solvent diffusion coefficient (Zellers and Sulewski 1993).

Solubility parameters vary within generic CPC materials due to the additives and manufacturing processes. In an attempt to compare the generic materials from different CPC manufacturers a proposal to introduce a test battery of specific permeation test chemicals to determine solubility parameters of CPC was put forward by Spence (1986).

Several models using three-dimensional solubility parameters have been developed. However, all have limitations as usually not all the information is available, for both the solvent and the polymer, due to reasons related to commercial secrecy (Zellers and Zhang 1993). Another important consideration is that there is not any allowance for other factors that are significant in permeation theory, and therefore empirical correlations are necessary. Que Hee (1996) argues that although these models adequately provide for adsorption it is difficult to explain the transition from adsorption to permeation. Elucidation of three-dimensional solubility parameters to glove studies is somewhat difficult to interpret because BT and L are both related to the diffusion coefficient and not solubility. However, they have been demonstrated as a useful model for multi-component liquids (Forsberg and Faniadis 1986).

3.7.2.6 Liquid-liquid partition model

This model has been designed to allow for the hydrophobic and hydrophilic components of different types of gloves by estimating the solute partitioning behaviour in various films (Que Hee 1996).

The majority of glove permeation studies uses solvents as the challenging chemicals, and these solvents are discussed in the next section, followed by an examination of pesticide permeation studies.

3.7.2.7 Solvent permeation studies

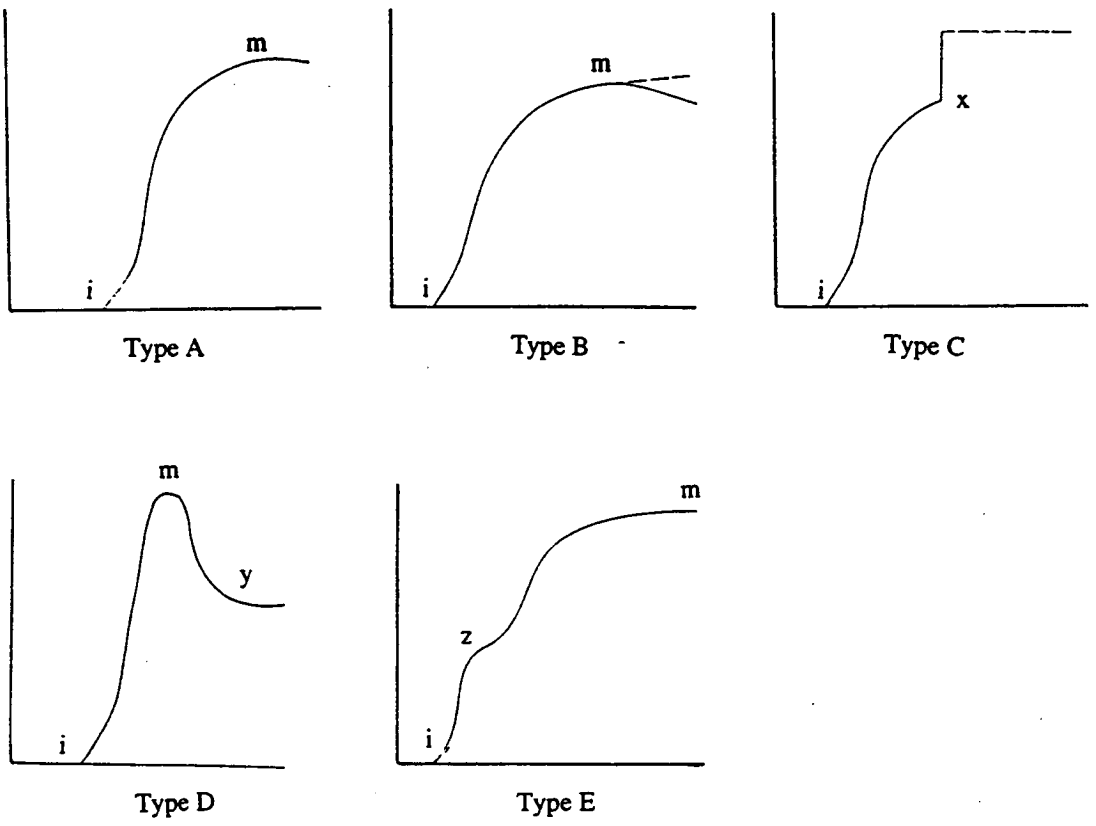
Solvents exert a mechanical action upon the macroscopic dimensions of plastics, but the primary polymer chain remains intact. If the polymer is in contact with a solvent in which one or more of the additives are soluble then they can be extracted from the matrix. This phenomenon is known as migration (Moisan 1985, pp.119–120), *e.g.* plasticiser migration from PVC.

Swelling of the surface may set up a stress that is relieved by crazing (Rodriguez 1982, p.282). This swelling and deformation not only influences the utility of the glove but also has an impact upon conventional permeation testing procedures. The uneven surface alters the sample surface area and intimate contact cannot be maintained when using a solid collection medium (Pinnette and Stull 1991), although this problem can be negated if suitable liquid or gas collecting media are used (Mikatavage *et al.* 1984), *e.g.* a gas cannot be used to collect a pesticide of low volatility (Harville and Que Hee 1989). However, it is unlikely in real life that a farmer would wear a deformed glove, similarly a researcher would note the deformation and would discontinue a fruitless and expensive task (Bodek *et al.* 1991).

Solvent permeation through several types of CPGs was reported to occur in serious quantities in an early study (Sansone and Tewari 1978). This was developed further by Nelson *et al.* (1981) who described five types of permeation behaviour in gloves by organic solvents (Figure 3.2). Moderate swelling of glove samples initially resulted in a normal permeation curve followed by a sharp decrease prior to reaching a state of equilibrium. Extreme swelling resulted in a double S shape permeation curve (Figure 3.2). Similar permeation profiles have been found with ethylene glycol dimethyl ether glove permeation (Menke and Chelton 1988).

FIGURE 3.2

Permeation behaviour as determined by Nelson *et al.* (1981)



Type A. The glove sample remains unchanged during the test, BT is at point i.
Type B. There is some chemical modification. The maximum is reached at point m and then there is stabilisation.
Type C. There is catastrophic breakthrough which occurs at point x and then the sample dissolves.
Type D. Equilibrium is at point y. There is moderate to heavy swelling or deformation of the glove.
Type E. There is an inflection at point z and very severe swelling of the glove.

Nitrile gloves challenged with individual chlorinated solvents altered the surface integrity by minor swelling and had differing BTs. A plausible explanation given was that the swelling gave rise to minor cracks and thus facilitated permeation (Mikatavage *et al.* 1984). However, this finding cannot be extrapolated to all solvent nitrile interactions. The swelling of NBR in response to propylene glycol monomethyl ether acetate challenge was reported by Zellers and Sulewski (1992). In this study NBR gloves exhibited the most severe deformation, although they had the highest permeation resistance.

An interesting study examining permeation of Viton® and NBR gloves by specific chlorinated solvents placed emphasis on thoroughly mixing isopropanol, the collecting medium, in an ASTM cell. The cell was clamped to a powered agitation tray that moved horizontally at 15 cm/sec. Both supported and unsupported gloves were tested. The NBR gloves had BT of less than one hour compared to the Viton® at greater than four hours, but the interesting point was that the NBR exhibited some swelling prior to BT. Nitrile rubber was immersed in isopropanol for four hours with no visible effects upon the sample's integrity. A plausible discussion followed where the researchers postulated that the swelling acted as a precursor to "microtears" and thus to shorter BTs (Mikatavage *et al.* 1984). However, the experimental conditions simulated those necessary for ESC by the chlorinated solvents as the attacking medium and tensile stress applied by the motion of the isopropanol against the NBR. An alternative, but more improbable scenario is that pseudo-cracking occurred during the experiment. Unfortunately the specimens were not analysed microscopically.

One of the landmark papers in glove permeation research is that by Mickelsen *et al.* (1986) where it was reported that permeation of mixed solvents may be greater than that of pure chemicals. Three observations were described. Firstly, decreasing BT of the components, secondly a component that under normal test conditions does not permeate may be transported with another component and thirdly a synergistic effect was noted. However, this is not always the case as a mixture of 30% ethylene glycol dimethyl ether with 70% propylene carbonate increased the BT of butyl gloves. The addition of propylene carbonate had an inhibitive effect upon the permeation profile of ethylene glycol dimethyl ether by significantly extending the BT (Menke and Chelton 1988).

Some researchers have conducted permeation studies on protective clothing incorporating the same techniques as glove testing. Composite materials exhibit different types of permeation behaviour depending upon which surface component is in contact with the challenge solvent. Sarenex® laminated Tyvek® was tested facing

both ways. Sarenex® exhibited Type A behaviour and Tyvek® Type C (Figure 3.2) (Stampfer *et al.* 1984). Sarenex® is a film laminate, (23-P) polyethylene, vinylidene chloride and vinyl chloride and Tyvek® is a non woven polyethylene. Both are trademarks of Dow Chemical Company and the materials are used for CPC (Forsberg and Mansdorf 1993, pp.97–98). Teflon® revealed inconsistent results when challenged with 1,2-dibromoethane and it was suggested that this was due to flaws in the material, which were exacerbated by thoroughly flexing the sample before placing it in the test cell (Stampfer *et al.* 1984). These flaws were illustrated with an electron micrograph and they may be associated with a brittle fracture. Teflon® is tetrafluoroethylene, a plastic like material with exceptional thermal and chemical resistance properties but inferior mechanical properties. Usually it is incorporated in the manufacturing process with materials to produce CPC (Forsberg and Mansdorf 1993, p.98).

3.7.2.8 Pesticide permeation studies

Most pesticides consist of several components such as the active ingredients, carrier solvents, surfactants and stabilisers. The exact nature of the formulations is regarded as proprietary information and is not available to the general public. The formulation of the pesticide is the most critical factor. There are several types of formulations, such as aqueous solutions and concentrates, wettable powders, dry flowables, granules and emulsifiable concentrates (Table 2.4). Exposure to aqueous and emulsifiable concentrates poses greater risks to workers and are more likely to permeate CPC. Pesticides containing organic solvents are most aggressive on gloves.

A pioneering study by Maddy *et al.* (1985) considered the transmission of pesticides through used gloves. Their methods involved a triple rinsing procedure, extraction with methylene chloride and analysis with mass spectroscopy followed by nitrogen phosphorus and electron capture gas chromatography. This is an important but rudimentary study as it established that pesticides can be detected from used gloves. There are several shortcomings in this paper, the authors failing to describe the types of gloves other than that they were impervious. This lack of information is also repeated in their pesticide descriptions as formulation types are not mentioned. A tentative conclusion that wearing gloves in certain conditions may increase the risk of exposure was made. This supposition was investigated by Moody and Nadeau (1994) and is discussed in the next paragraph.

Some pesticides are able to reside within the polymer matrix and thus this combination may function as a reservoir and potentially increase the risk of exposure over time (Perkins *et al.* 1987). Measurement of this effect to portray real life situations is

somewhat difficult. A major obstacle is finding a solvent with an extraction efficiency that mimics real life. A comparison of NBR permeation of C-radio labelled 2,4-D-DMA, DDT, DEET and diazinon diluted with acetone to spiked neat formulated commercial products determined that there was a substantial reservoir of the active ingredients in the acetone diluted group. This finding is, of course, not absolute because analysis was with liquid scintillation counting. Therefore, only the spiked active ingredients in the formulated products are accounted for and the transport and/or displacement of the real active ingredients is not known. Methanol was used to extract the active ingredients from the gloves after washing in soapy water followed by a distilled water rinse (Moody and Nadeau 1994). Unfortunately this study did not examine pesticides diluted to meet application conditions, but did demonstrate the reservoir action. This phenomenon has also been supported by some solvent permeation studies (Zellers *et al.* 1992; Zellers and Sulewski 1992).

In an attempt to simulate field conditions, 2,4-D isooctyl ester was tested at the formulation concentrate and at the highest recommended dilution rate for application on several types of NBR and neoprene gloves. The concentrated formula affected NBR by causing swelling for both the unsupported and supported and unlined and lined gloves, but no swelling was observed for the diluted formula. The permeation behaviour was representative of Type B for the neoprene and Type E for the unsupported NBR (Figure 3.2). It was stated in this paper that the materials that exhibited physical changes after pre-conditioning in a desiccator were assessed microscopically, although this is not elaborated upon. An *ASTM F739-85* method was employed using hexane as the collecting medium that did not have any effect on NBR. One of the exciting findings in this study is that following BT from the concentrated formula there was no further evidence of permeation, although this was not so with the diluted formula (Harville and Que Hee 1989). This is an interesting study as it succinctly highlights some of the difficulties that bedevil the agricultural worker or adviser when faced with choosing suitable CPGs.

A comprehensive review of pesticide glove permeation was conducted by Schwope *et al.* (1992). They developed a qualitative rating system based upon the BT of various carrier solvents. Their own permeation testing method was the same as that described by Ehntholt *et al.* (1989). Permeation behaviour of active ingredients and carrier solvents were monitored. The parameters measured were: the BT of the a.i. and the carrier solvent plus their cumulative rate of permeation for an eight hour time period. Their results indicated a general trend where the cumulative carrier solvent permeation was much greater than that of the a.i. This was true for approximately two thirds of this rather large study, which monitored the a.i. and carrier solvent permeation through

thirteen types of CPGs in one hundred permeation tests in triplicate. Trends for BT were not so distinct, with just over half of the sample recording equal BT for active ingredients and carrier solvents for twenty different pesticide formulations. Carrier solvents had a shorter BT than active ingredients in approximately a quarter of the sample. The remainder, which were mainly composed of NBR, butyl rubber and Silver Shield™ indicated that active ingredients had a shorter BT than carrier solvents. The latter also had relatively low permeation rates at $<100\mu g/cm^2$. Silver Shield™ is a trade name for the North Company and is a film laminate of polyethylene and ethylene vinyl alcohol copolymer (Forsberg and Mansdorf 1993, p.98). The conclusion reached was that generally there was good agreement between BT time trends for neat solvents and pesticide formulations. This study is put forward as a preliminary guide for those involved in the selection of gloves for pesticide use in the absence of a more sophisticated guide. The limitations of using BT as an indicator for CPG efficiency have been previously discussed and therefore this study has severe limitations for field application.

Ehntholt *et al.* (1989) developed a testing procedure based upon a modified *ASTM F 739-85* method with silicone rubber as the collection medium. This procedure allows for simultaneous permeation testing of volatiles, non-volatiles and low water solubility components in some commercial OP formulations. The general, but not absolute, finding was that the carrier solvents permeated more quickly than the a.i. and in much higher concentrations, irrespective of their ratio within the commercial formulae. The validity of this study was disputed by Pinnette and Stull (1991) because in a replicate test they found that the solid collection medium did not maintain intimate contact with the specimen and therefore this procedure was subject to gross underestimation. They also expressed some concerns about the faster permeation of the carrier solvents compared to the a.i. permeation because of their inherent differences as current scientific opinions suggest that smaller molecules permeate at a greater rate than larger homologues. The active ingredients in question were ethyl parathion and methyl parathion and their molecular weights were regarded as insignificant compared to the xylene induced permeation differences (Bodek *et al.* 1991). The higher xylene aromatics resulted in earlier BT and higher permeation rates (Ehntholt *et al.* 1989). This effect was supported by Moody and Nadeau (1994) who observed xylene enhancement of permeation of diazinon through NBR gloves. Other researchers have examined the relationship between the solvent in formulated pesticides and the solute permeation rates. On some occasions the solute permeated at a much faster rate (Watkinson *et al.* 1993).

It is common practice for farmers to use their gloves for more than one type of pesticide or for mixed pesticide applications (personal observation). Lipophilic DDT and hydrophilic 2,4-D were tested with DEET (N,N-dietyl-m-toluamide) for their permeation properties on natural rubber gloves, and although DEET permeation occurred there were no significant effects from the addition of DDT or 2,4-D (Moody and Nadeau 1992).

There are very few studies that report visible effects on the polymer following pesticide exposure. Moody and Nadeau (1994) noted that diazinon in a commercial formulation containing xylene had a corrosive effect on NBR gloves.

This section has explored permeation testing and theory and the next section examines penetration of chemicals through glove materials.

3.7.3 Penetration testing

Penetration is the transmission of a chemical through pin holes, imperfections, seams and tears (Ansell Edmont 1990). The purpose of penetration testing is to reflect the bulk flow of the chemical through the material or its potential to do this. The principal test for penetration is the air leak test. This rather simple but effective test involves inflating the glove, immersing it in water and inspecting it for air bubbles. Glove thickness determines the amount of air pressure used as stated in the *BS EN 374-2: 1994*. The second type of test is the water leak test, which involves filling the glove with water and checking for leaks. Talcum powder or blotter can be used to enhance visual confirmation. Both of these tests prescribe that the challenging chemical contacts the exterior of the glove material and observation is made through a port so that the interior of the glove surface can be visualised. The testing procedures are outlined in *BS EN 374-2: 1994*. These tests are representative of field conditions in the form of splash and spills. Generally, the materials that resist chemical permeation also resist penetration and failure is due to tears, holes and manufacturing processes (Stull and White 1992). Penetration of chemicals through CPC is increased in areas that contain seams and closures and therefore these are the weakest part of the garment (Berardinelli and Cottingham 1986).

A test method which involved spraying whole gloves was developed to determine penetration and was compared to patch permeation tests. In this study both tests were comparable and therefore it was assumed that the gloves surfaces were invariable (Williams 1981). However, the gloves were only sprayed for one hour and although permeation did occur it may not have been long enough or droplets may have been at the wrong angle for penetration to occur. In a study of simulated diazinon splashes on

various microporous fabrics it was concluded that the uniformity of the water repellent finishes was related to the amount of sorption (Shaw and Hill 1990).

Pinholes can often go undetected for considerable periods of time (Ringo *et al.* 1984; Williams 1994). A hole in a glove has idiosyncratic characteristics governed by the glove material, the thickness of the material at the hole perimeter, and its diameter. Recognition of the hole is dependent upon the surface tension and the flow rate of the air or water. When these characteristics are taken into account with the penetration test method it can be represented by equation 12 (Carey 1994):

$$P \approx 1.1 / R \qquad (12)$$

where P is the water pressure mmHg and R is the curvature of the droplet as it progresses through the hole. In order for a hole to be detected, the value of P must be greater than the smallest radius of the drop as it moves through the hole. Therefore the critical pressure is directly related to the hole size and the contact angle between water and glove. This process can also be adapted for the air leak test.

An inter-laboratory study to assess validity of the *ASTM F-903* concluded that there was a relatively high degree of agreement in the results. This study included seven laboratories analysing the same CPG materials and Tyvek® against the same liquid challenges, all of which were provided by the same supplier. There were some areas of disagreement, but these may have been related to the level of inflation required, lack of clarity in the description of what actually constituted a droplet, or to flaws in the materials (Mansdorf and Berardinelli 1988).

Penetration testing is much more advanced and technologically superior in the surgical latex glove field. Medical glove monitors measure the electrical resistance from a circuit formed by the glove, medical officer and client. The fundamental principle underpinning this test method is that when a pinhole is formed it is filled with bodily fluid, which acts as an electrical conductor, lowering the resistance and triggering an alarm. This system is not fail-safe as hydration of the natural latex can readily occur, which decreases the electrical resistance and therefore it can lead to false positive readings (Williams 1994). This method cannot be readily applied to agricultural workers using pesticides wearing CPGs.

The next section examines degradation testing of CPGs.

3.7.4 Degradation testing

Degradation can be measured by several parameters that include elongation weight, thickness, tensile and tear strength of the glove polymer and simply by visual inspection. These methods of testing are relatively inexpensive to perform and are often used to initially determine polymer suitability for specific chemicals. Elongation is usually measured by hanging weights from the specimen before and after immersion.

Given the relative ease of degradation testing it does have surprisingly low profile in the glove literature, although it was demonstrated in an inter-laboratory study that quantifying these parameters is fraught with difficulties and reliability and validity of conclusions are major dilemmas (Coletta *et al.* 1988).

Some of the few pesticide polymer degradation studies are outlined below.

A comparative study that examined the qualities of a modified *ASTM Draft Test Method for Evaluating Protective Clothing for Resistance to Degradation by Liquid Chemicals, NIOSH 200 -84 0-2702, DEG, Revision 3, 6-5-86* and a test method developed for the American Coast Guard; *Chemical Resistance to Three Candidate Materials for the U. S. Coast Guard's Hazardous Chemical Protective Ensemble,* submitted a rapid, easy and economical degradation test method. The two test methods were comparable for weight but not for elongation. It was also noted that degradation was a function of time when comparing one and three hour exposures.

The differences in elongation were mainly due to different techniques. The *ASTM* method prescribed the use of a weight that would allow for a 20% elongation of the unexposed polymer specimen, which is frequently between 300–500 gm, and the Coast Guard Method which had a set weight of 150 gm for the unexposed specimen. These weights are then applied to specimens that have been exposed to specific chemical challenges and the percentage of elongation can be calculated. In the unexposed specimens elongation is slight when the 150 gm weight is used and this makes comparisons between the two methods very difficult.

These researchers tested several CPGs for degradation against various pesticide formulations. A general observation indicated that degradation was greatest in NR, neoprene, NBR and PVC against the pesticides containing light aromatic petroleum distillates as their carrier solvents. Several classes of OPs were used in this

experiment, but the weight increase of the CPGs was dependent upon the amount of xylene in the formulation and not the formulation characteristics (Ehntholt *et al.* 1987).

A comparative study to assess the tensile strength and the puncture resistance of NBR and neoprene, with and without additives, was conducted to assess the protective properties of these glove materials if they were caught in moving mechanical parts. The tensile strength tests utilised three parameters: elongation; draw tension at breaking point; and the modulus, which is the ratio of stress to strain. The results of neoprene with and without additives were similar. However, the NBR without additives did less well than the NBR with additives in the elongation and breaking point tests. Overall, the modulus for elasticity was higher for the NBR, and in particular the NBR with carbon and chlorination that had been latex dipped. The results of the puncture tests indicated that the neoprene samples were too elastic to measure force of breakthrough in the puncture resistance tests and the latex dipped NBR were the most resistant (Forsberg *et al.* 1986)

Weight and volume changes are indicators of solubility and are usually measured before and after twenty-four hours immersion in a specific chemical. An attempt was made to correlate the log of these changes with the log of normalised BT for several CPGs and four organic solvents. Fairly good correlations were reported but they acknowledged that there was no theoretical justification for them (Stampfer *et al.* 1984). Weight and volume changes were used to predict BT by simple regression analysis and by discriminate analysis, the latter being the preferred method and was adapted for predicting permeation rates (Stampfer *et al.* 1988).

Raheel and Dai (1997) tested PVC, NR, disposable latex, NBR, butyl, neoprene and Viton™ gloves for degradation by immersion in 0.5% liquid solutions of carbaryl and atrazine for eight, sixteen and eighty hours. The parameters they measured were weight, thickness, flexural rigidity, puncture resistance, breaking load, elongation and chemical penetration. All the gloves passed the penetration tests. The NBR, Viton™ and butyl gloves had superior chemical penetration resistance properties. Butyl and Viton™ were unaffected by the immersions. The NBR and neoprene gloves were fairly resistant to change until after sixteen hours exposure. The NBR gained very little weight and had a slight increase in thickness whereas the neoprene gloves showed a slight weight increase and a decrease in thickness. Their results showed that PVC gloves progressively increased in weight and this correlated well with an increasing thickness for carbaryl but not atrazine immersions. These gloves became limper and had increased puncture resistance. There was a decrease in breaking load and elongation following immersion in carbaryl, but the opposite occurred following

atrazine immersion. This indicated that there was some diffusion of the chemicals into the material. The latex gloves became plasticised during the immersions and this was demonstrated by a decrease in weight and thickness, limpness, high puncture resistance and elongation.

The effect of glove flexion on BT and SSPR was assessed by immersing gloved human hands in sealed test chambers containing heptane or acetone and flexing the hands thirty to fifty times per minute. The hands were covered in four types of gloves to prevent perspiration contamination, protect the employee and to allow for air circulation. The outer gloves were either PVC, that was exposed to heptane, or neoprene, that was exposed to acetone. They assessed BT by weight loss versus time and assessed SSPR from the exposed glove area and the slope of the weight versus the time line. It was reported that the PVC heptane experiments showed a decreasing BT and increasing SSPR with time, or the frequency of flexion. The neoprene acetone experiments also showed decreasing BT and increased SSPR against the un-flexed gloves, but the number of flexes did not influence these parameters. It was therefore concluded that glove flexion does influence the permeation profile of gloves, which is an extremely important finding for gloves used in agriculture (Perkins and Rainey 1997).

During a herbicide glove permeation study substances not intrinsic to the commercial formula were detected in the collecting medium, indicating that the glove materials, NBR and neoprene, underwent some degradation and/or contamination (Harville and Que Hee 1989).

Degradation was observed in neoprene specimens during a study assessing chlorine, hydrogen cyanide and formaldehyde permeation through NBR, neoprene, NR and butyl rubber. The neoprene became brittle following eight hours continuous exposure to 0.1% chlorine gas. Exposed and unexposed neoprene specimens were examined at 100 x with a scanning electron microscope and the exposed specimens were described as having "linear raised cracks with irregularly shaped platelike structures". The surface integrity had certainly been compromised although BT had not occurred. However, in real life the brittleness of the neoprene may cause failure when flexion occurs and may be uncomfortable. Natural rubber specimens exposed for six continuous hours to 37% formaldehyde had BTs >8.0 minutes, developed "pronounced nodules protruding inward toward the inside surface of the glove". Unfortunately, the illustrating photograph is not very clear and it may be possible that these are cavities (Henry 1986, pp.53–55).

These methods provide useful preliminary tools to decide which materials can be rejected.

Comfort and durability of CPGs are important issues that affect compliance and are addressed in the next section.

3.8 Factors Influencing Glove Use

3.8.1. Comfort

Comfort is entirely a subjective criterion incorporating numerous physiological and psychological domains. The discomfort of protective clothing is primarily related to thermal insulation and water vapour resistance, factors that are exacerbated in tropical climates (Chester *et al.* 1990). Other factors include fit, weight, flexibility, tactility and contemporary fashion modes (Akbar-Khanzadeh *et al.* 1995). Grip function of neoprene is superior to that of NBR gloves (Stone *et al.* 1994). Akbar-Khanzadeh *et al.* (1995) found that only 42% (n = 95) of workers in an automobile encapsulating plant rated rubber gloves as comfortable.

A critical point is that the use of protective clothing decreases work performances and increases the task performance time (Mansdorf 1994; McLellan 1993; McLellan *et al.* 1993a; McLellan *et al.* 1993b; McLellan and Frim 1994). Wearing CPGs decreases abduction, adduction, supination and pronation but does not alter extension or flexion (Bellingar and Slocum 1993).

The glove fit also plays a significant role in dexterity. A glove that is one size too large significantly reduces dexterity, whereas too small has little effect (Bellingar and Slocum 1993; Tremblay-Lutter *et al.* 1994). However, gloves that are too small are restrictive and make the hands tire more readily (Ness 1994, p.55).

3.8.2 Durability

Stone *et al.* (1994) noted that replacement of gloves by pesticide operators was seasonal or when a leak was detected. In a waste processing plant it was reported that workers replaced their PVC gloves daily because of the residual odour (Bromwich *et al.* 1994–1995, P.70).

Chester *et al.* (1990) reported that NBR was robust enough for tropical situations although replacement was necessary due to splitting and abrasion. This study was far too small to formalise realistic conclusions, and there were some major drawbacks in as much as the glove specifications, such as thickness, were not recorded. Glove

thickness was found to be inversely proportional to visible glove failures in a study investigating manual dexterity when wearing CPGs (Bensel 1993).

3.8.3 Compliance and barrier perception

Generally, farmers believe that gloves provide an adequate barrier against farm chemicals (Chester *et al.* 1990). Weisskopf *et al.* (1988) conducted a study on pesticide applicators who were using diazinon in a Japanese beetle eradication program. They reported that the personnel used rubber gloves and that they required three to four pairs of gloves for a six day working week. The reason the gloves were changed so frequently was that they became dirty and/or torn, but unfortunately no further details were given.

In a comparative study of commercial pesticide applicators' and growers' attitudes and practices towards PPE it was reported that the growers who used the more toxic pesticides also perceived the risk of pesticide exposure to be less (Rucker *et al.* 1986). Unfortunately, this study did not examine CPG use. Ramaswamy and Boyd (1991) concluded that compliance for using PPE was related to knowledge and education levels, although glove use was not a specific objective and only a small percentage of the respondents wore gloves.

In a small Australian study, most farmers stated that they always read the safety advice on the labels prior to use, including withholding periods, but many did not calibrate their equipment and fewer than half of them wore water resistant gloves (n = 28). The reasons for not wearing CPC included discomfort and generally too hot and too heavy (O'Connor 1991). There was a high compliance rate for wearing rubber gloves when indicated on the pesticide container label among industrial pesticide applicators (Popendorf *et al.* 1995).

In the Philippines, workers who used knapsack sprayers for rice crops did not wear gloves and the dorsal hand surfaces were contaminated as were their backs from leaking knapsacks (Van Sittert and Dumas 1990). Ambridge *et al.* (1990) noted that farmers in tropical climates were less likely to wear complete CPC during spraying, with approximately 50% of their body surface unprotected, mainly head, legs and arms. As well their post application hygiene was poor. Pesticide applicators in Sri Lanka were reluctant to wear PPE, because of discomfort, even though they had knowledge and experience of the dangers of pesticide toxicity (Sivayoganathan *et al.* 1995). This finding was supported by Desi *et al.* (1990) who noted that women who worked in greenhouses wore bathing suits and rubber gloves. In a farm audit study in

South Africa it was reported that the availability of PPE was reasonably high but the actual use of masks and gloves was very low (London 1994).

In a British report thirty-two cases of adverse reactions to sheep dipping agents were discussed in relation to the PPE used. In only three cases was full PPE (bib-apron waterproof jacket and rubber gloves) worn. Partial or unsuitable PPE was worn by twenty people, which included no gloves or unsuitable gloves, two people did not wear any PPE, and information was unavailable for the remaining four (Veterinary Medicines Directorate undated).

3.8.4 Factoring in the environmental issues

In real working situations CPGs encounter numerous environmental agents, which pertain to storage, maintenance and use. There is a paucity in the literature of these issues.

A simulation study examining the storage of CPC materials in dark versus light conditions suggested that after one month there were virtually no significant differences in permeation profiles against the selected solvents (Sansone and Jonas 1981b)

Moody and Nadeau (1992) established that permeation of 2,4-D (2,4-dichlorophenoxyacetic acid) in NR gloves was augmented with exposure to UV-A but had no effect with DDT. Photo-enhanced permeation was observed in a similar study with NBR and NR but with no effect on PVC (Moody 1992). In these studies the UV-A (350 nm) exposure took place within the test cell within various time limits. To determine if the effect was associated with ozonisation, the permeation test method was tried with nitrogen rather than air. Since this demonstrated no photo-enhanced permeation, it was presumed that this observation was indeed related to ozonisation (Moody and Nadeau 1992).

In an attempt to simulate real life situations by air drying the gloves for twenty hours in between conventional permeation testing Forsberg and Faniadis (1986) found no effects. These gloves were not subjected to the rigours of real life working situations and therefore it is difficult to make a firm conclusion.

3.8.5 Risks associated with wearing chemically protective gloves

It cannot be assumed that wearing gloves provides a completely hazard free situation. The hazards are intrinsic and extrinsic. Intrinsic factors are related to the glove constituents themselves. For example, some of the phthalic plasticisers are

carcinogenic and teratogenic, specifically bis(2-ethyl hexyl)phthalate. Many cases of allergic responses to proteins in latex rubber have been reported in the literature (Kanerva *et al.* 1994; Kaniwa *et al.* 1994; Siler and Cornish 1995). When dissociation, migration and other physical mechanisms occur there is a real risk of exposure.

Extrinsic factors are the known risks of the chemicals in combination with physiological factors. Typical dermal physiological defences are overwhelmed when faced with an impermeable barrier, *e.g.* wearing occlusive gloves enhances absorption of available chemicals (Aoyagi *et al.* 1994; Ness 1994, p.52). The response of the stratum corneum to occlusion is hydration and maceration because evaporation is inhibited and in this condition xenobiotics readily penetrate (Graves *et al.* 1995). Humidity is increased by occlusion and this is a dynamic parameter that influences dermal absorption of pesticides. Usually, increasing hydration and humidity favours absorption of polar compounds although absorption of non polar compounds, such as parathion, also increase (Chang and Riviere 1993). Occlusion of the skin inhibits volatilisation of volatile OPs, such as parathion, and therefore increases the amount of pesticide available for absorption. Not only has occlusion been found to enhance the absorption of parathion but also to facilitate transport through the skin into the circulatory system (Qiao *et al.* 1993). Increasing the surface temperature of the skin by occlusion augments vasodilatation and therefore can decrease evaporation of the pesticide or solvent thus increasing absorption (Chang and Riviere 1993).

It is conceivable that perspiration may have a significant influence upon the protective properties of gloves. Lined gloves may become saturated with perspiration and consequently pesticide transport may be rapid through capillary action. This is of course dependent upon the glove structure, the volume and pH of the perspiration and the formulation of the pesticide. Various types of fabrics immersed in synthetic perspiration exhibited increased transportation of pesticides (Raheel 1991).

The way gloves are worn may influence the degree of risk. For example, if a person wears gloves over coverall sleeves it increases the likelihood of chemicals spilling down the inside of the gloves and thus contaminating the skin. One of the conclusions put forward in an autopsy report of a farm worker who had been applying a granule formulation of aldicarb was that the death may have been related to the granules falling inside the gloves (Lee and Ransdell 1984). Another possible problem can occur when the external surfaces of CPGs become moist, since the grip function may be compromised and increase handling difficulties (Leinster *et al.* 1990). Short-term use of barrier gloves does damage the stratum corneum temporarily. Recurrent use may

have a cumulative effect and may have long-term effects upon the barrier properties of the stratum corneum (Graves *et al.* 1995).

3.9 Chapter Summary And Conclusions

This chapter has addressed some theories from polymer science and their relevance to the efficacy of CPGs. Some indices and their shortcomings have been described such as BT, permeation rate, the solubility of the challenging chemical and diffusion coefficient, which are all mathematically related. Other factors such as weight and volume changes that are a function of solubility have been covered.

All the test methods have limitations that are dependent upon a range of parameters such as analytical sensitivity, glove surface variations, the chemical glove interactions and the reporting procedures. Considerable diversity and disagreement are evident in the field of permeation testing research. However, it should be encompassed in the overall scenario where statistically significant differences become less important for practical purposes, but what is important is that the rank order is the same when comparing permeability data. There is a great variety of glove testing methods and procedures, which indicate that the field of CPG science is still rapidly developing and requires much more research. It is also apparent that it is impossible to make effective comparisons for testing procedures and currently the tests should be used symbiotically to assist the end user to make an informed choice of glove type. Minimal research has been done on the barrier properties of CPGs associated with pesticide use. It is noteworthy that there is a great deal of interest in the cracking and crazing in polymer science, but this interest has not spilt over into CPG research. Usually cracks are mentioned as an incidental phenomenon. The research in this thesis is primarily dedicated to the surface topography of new and used gloves suitable for agricultural pesticide work and therefore attempts to fill this knowledge deficit.

Chapter Four

Macroscopic Assessment Of Chemically Protective Gloves Used In The Agricultural Sector

4.1 Introduction

Although there has been a variety of research conducted on the efficacy of CPGs, very little has been targeted specifically at agricultural workers' gloves. It has been difficult to ascertain what types of gloves Australian agricultural workers are wearing when applying pesticides, although many pesticide containers have instructions on the label that recommend applicators wear "impervious gloves" to minimise dermal exposure. Usually there is no guidance as to what type of gloves should be worn or how they should be maintained.

The aims of this study were:

1. to determine what types of gloves were being used by agricultural workers when they apply pesticides;
2. to determine the typical condition of the used CPGs;
3. to determine the average age of the used CPGs; and
4. to assess the on-farm maintenance of CPGs including storage and cleaning.

4.2 Materials And Methods

A replacement glove program was instigated where agricultural workers were issued with new gloves of their choice when they handed in their used gloves. The information about the program was disseminated by short informative articles published in the *Tasmanian Country,* a state-wide rural newspaper, *The Huon News,* a regional newspaper based in a rural horticultural area, and by direct contact with some agricultural retail outlets and the Tasmanian Department of Primary Industry. The major rural retail and safety equipment outlets were visited to determine which were the main types of gloves sold to farmers by interviewing the specialist sales personnel. The rural retail outlets visited were Roberts Pty. Ltd., Servag, Websters Pty. Ltd. and UMT Hopkins. The safety outlets visited were Eastside Agencies, MSA Pty. Ltd. and Protector Safety. Two organisations were directly approached as they had a large body of employees. The Grove Research Station, which is a State Government farm specialising in apple growing, and Tahune Fields that is part of a large organisation specialising in training for the intellectually disabled. Both of these farms are located in the Huon Valley. Tahune Fields is a diverse horticultural enterprise growing various plants including apple tree seedlings, cherries and roses and has satellite farms located at several sites in the Huon Valley. Several farm apprentices are employed there. Workers at Tahune Fields are encouraged to use a double gloving technique when using chemicals, wearing NBR next to the skin and PVC outside. However, when the farms were visited some of the workers were observed wearing the NBR gloves without the PVC gloves.

A simple questionnaire was designed and tested for clarity on six farmers and ten students from the University of Tasmania. The questions related specifically to the glove history, age, chemicals used with the gloves, whether they were stored in the dark or in the light and whether they were unwashed, or washed in water, or washed in water and detergent. The gloves were collected by the candidate or left at a depot arranged with Roberts Pty. Ltd.

4.2.1 Scoring the data

The gloves and their corresponding questionnaires were coded according to farming origin and the data were entered on a spreadsheet (Microsoft Excel 4, 1992). The gloves were categorised according to their materials, polymeric or elastomeric families, and the entire glove surfaces were visually examined to assess their condition. The observed failures were cracks, splits, macropores, abrasions and punctures. Visible cracks were defined as failures that did not penetrate through to the internal surface, whereas splits extended from the exterior to the interior surfaces (Figures 4.3 and 4.4). Macropores are usually related to the manufacturing process, particularly in PVC. Punctures generally had well-defined edges and it was apparent that they had been caused by a puncture or stab type injury. Abrasions could be easily seen as failures caused by rubbing or friction. These failures were measured with a ruler and their location and size recorded. A glove template was made and divided into sections that were coded to provide a systematic method to record the locations of the failures. The coded template was represented as: T = thumb; F 1 = index finger; F 2 = middle finger; F 3 = third finger; F 4 = little finger; TT 1 = thumb tip; FT 1 = index fingertip; FT 2 = middle fingertip; FT 3 = third fingertip; FT 4 = little fingertip; A = thumb web; B = index/middle finger interstice; C = middle/third finger interstice; D = third/little finger interstice; P = palm; and DO = dorsal surface.

4.2.2 Statistical analyses

Failures in the PVC gloves were not normally distributed (Kolmogrov-Smirnov Test) and therefore the non parametric Kruskal-Wallis One way Analysis of Variance (ANOVA) on ranks was performed. The statistical program Sigmastat™ (Jandel Scientific 1994) was used. There were only two types of NBR gloves collected and their failures were not normally distributed, consequently a Mann-Whitney Rank Sum Test was conducted. The natural rubber (NR) gloves were combined because there was only one type of unsupported NR glove, which was in the BG group and as it was the only elastomer within this group its identity would not be hidden. Failures were not normally distributed and were analysed in the same manner as the PVC gloves. The leather/cotton and leather gloves were combined, their failures were normally distributed and therefore a t test was conducted. The Solvgard™ and the thin

PVC were too few to warrant analyses and descriptive statistics have been used. The maintenance factors could not be compared as they were confounded.

4.3 Results

The best selling CPGs to rural workers were the PVC gloves, which were supported with cotton knit and were manufactured in China. All the PVC gloves were red with the exception of one pair of black gloves, also made in China. This was unanimously confirmed by the retailers and this trend is reflected by the quantity of PVC gloves collected in comparison to other types (Table 4.1). The black PVC gloves were slightly smoother than the red, with less tacky surface, and did not have as many inclusions. There were three thin unsupported PVC gloves collected. The majority of the NBR gloves were Sol-Vex™ manufactured by Ansell Edmont with a few from MSA. The PVC/NBR (Solvgard™) were manufactured by MSA Pty. Ltd. The NR gloves collected were unsupported washing-up gloves from the BG group and supported Hy-Care™ gloves from the OR and TF groups, and both were manufactured by Ansell Edmont. Figures 4.1 and 4.2 show some of the new and used gloves from the exchange program.

A grand total of eighty-six gloves were collected and of these only thirty-one gloves were intact. Gloves were coded according to their owner's current farming enterprise and by the polymeric and/or elastomeric formulation and other materials (Tables 4.1 and 4.2).

TABLE 4.1

Classification of agricultural workers' gloves by type

Glove type	Quantity
PVC	48
NBR	17
NR	10
Thin PVC	3
Leather	4
PVC/NBR	2
Cotton/leather	2
Total	86

TABLE 4.2

Codes for glove origin ascertained from their working history

Farm category and region	Farming enterprise	Code	Glove quantity
Tahune Fields (Huon Valley)	Mixed horticulture	TF	42
Orchard farms (Huon Valley)	Apple orchard	OR	26
Derwent Park (Midlands)	Sheep grazing	DP	10
Botanical Gardens (Hobart)	Ornamental horticulture	BG	6
Vegetable farm (North West Coast)	Vegetable Growing	V	2
Total			86

FIGURE 4.1

Selection of new gloves. From left to right, washing-up glove, Hy-Care™, Sol-Vex™ (Ansell Edmont), black PVC (MSA), NBR, Solvgard™ (MSA), red PVC (made in China). Note the straight hand form of the red PVC gloves compared to the contoured hand forms of the others.

FIGURE 4.2

Selection of gloves collected from farmers in a glove exchange program
From left to right, leather, cotton/leather, washing-up, Hy-Care™, Solvgard™, Sol-Vex™, NBR (MSA), black and red PVC (made in China)

FIGURE 4.3

Split on a used red PVC glove

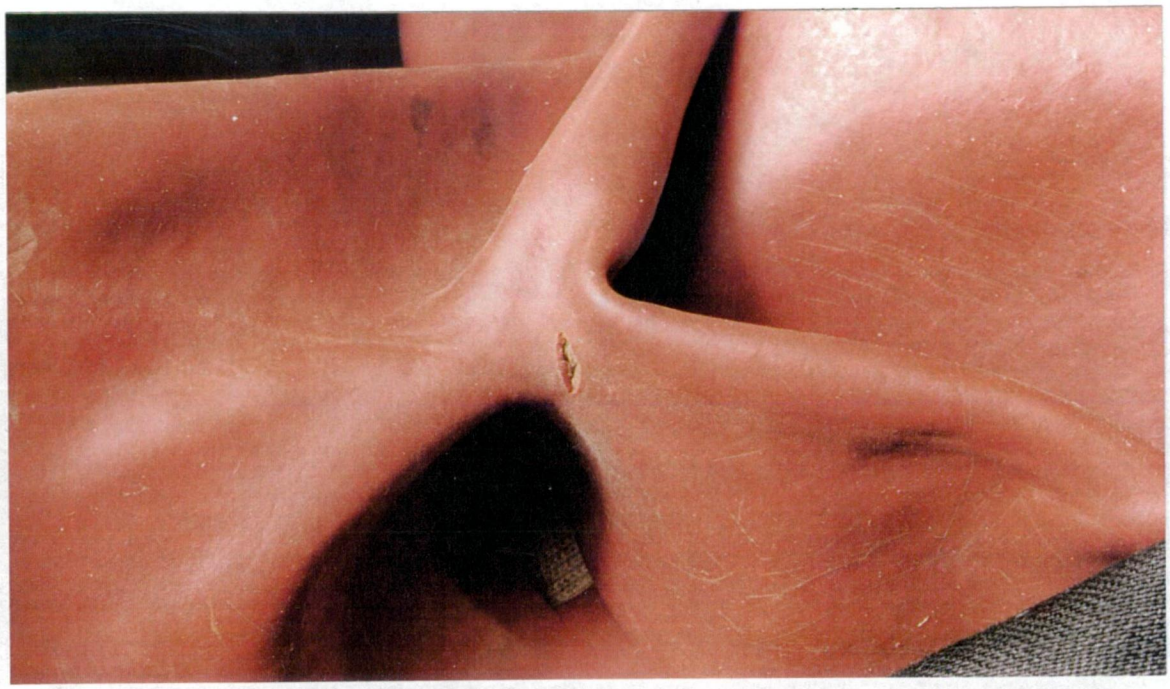
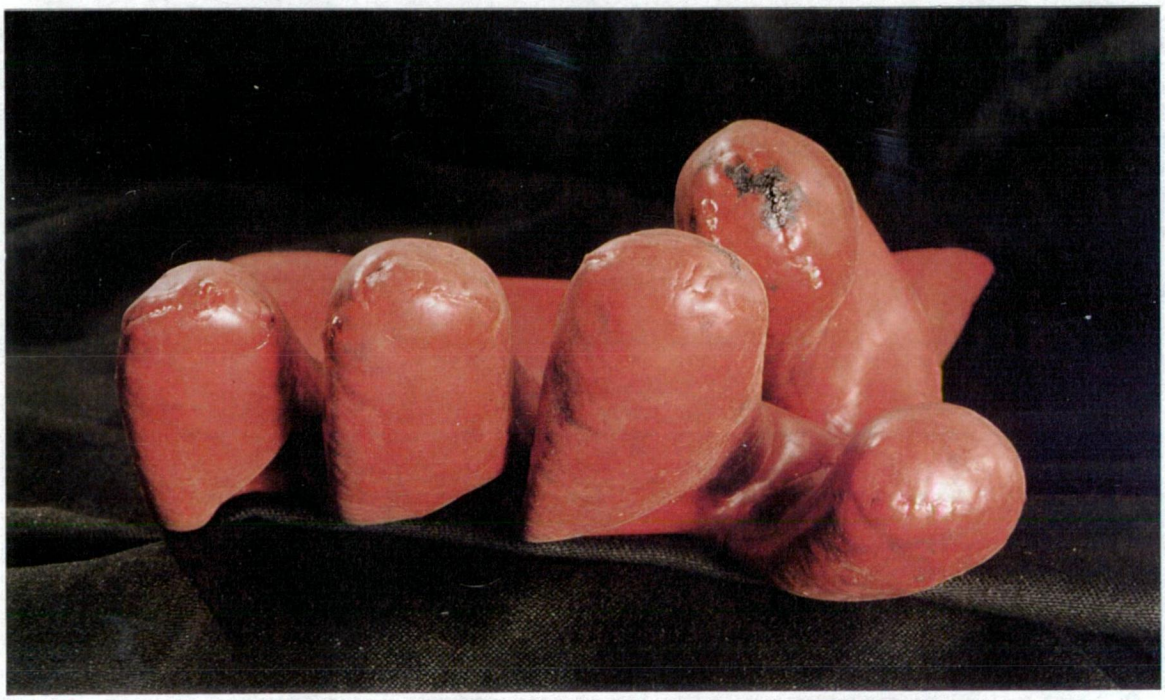


FIGURE 4.4

Cracks on a used red PVC glove



4.3.1 Polyvinyl chloride gloves

The data for the black and red PVC gloves were aggregated. Cracks, splits, macropores, abrasions and punctures were failures found on the PVC gloves. However, the origin of the gloves had no influence upon the pattern of failure: abrasions (H = 1.29, d.f. = 3, P = 0.7325); cracks (H = 7.64, d.f. = 3, P = 0.0541); macropores (H = 4.02, d.f. = 3, P = 0.2588); punctures (H = 1.76, d.f. = 3, P = 0.6229; and splits (H = 1.89, d.f. = 3, P = 0.5954). However, there were differences between the origins for the intact gloves (H = 11, d.f. = 3, P = 0.0118), as summarised in Table 4.3. The locations and mean sizes of the failures are summarised in Table 4.4.

TABLE 4.3

Intact PVC gloves and the inter-comparisons from various origins (Dunn's method following Kruskal-Wallis one way ANOVA on ranks). The medians are shown with the 25th and 75th percentiles. Probabilities are that the medians are significantly different. NS = not significant.

					Origin		
Origin	**n**	**Median**	**25%**	**75%**	TF	OR	BG	DP
TF	21	0	0	1				
OR	13	1	0	1	NS			
BG	4	1	1	1	NS	NS		
DP	10	1	1	1	NS	NS	NS	

TABLE 4.4

Distribution and location of failures in farmers' PVC gloves. The codes are: T = thumb; F 1 = index finger; F 2 = middle finger; FT 2 = middle fingertip; A = thumb web; B = index/middle finger interstice; C = middle/third finger interstice; D = third/little finger interstice; P = palm; DO = dorsal surface; and NM = not measured.

Failures	**Number of failures**	**Distribution and location**	**Mean size (mm)**
Abrasions	1	1 P	NM
Cracks	13	4 A, 7 C, 2 T	2
Macropores	22	1 C, 20 D, 1 P	1
Punctures	10	6 A, 2 B, 1 F2, 1 T	10
Splits	16	2 A, 2 B, 5 C, 4 D, 1 F1, 1 P, 1 T	6

The maintenance histories of the farmers' PVC gloves are detailed in Table 4.5. The mean age of the PVC gloves (n = 28) was two years. The age of the gloves was unknown for the TF gloves (n = 21), but all had been washed in water and detergent and were stored in open shelves in the light. The gloves from the BG group were in very good condition and had been washed in water and detergent, and stored in a dark locker. The DP 1–8 gloves had been stored on the floors of trucks and therefore were exposed to light. The DP 9–10 gloves had been washed in water and detergent and stored in the light.

TABLE 4.5

The range of maintenance of farmers' PVC gloves (n = 48) from the exchange program

Maintenance factors	%
Unwashed	22.9
Water washed	4.2
Water and detergent	72.9
Dark storage	20.8
Light storage	72.9

The only comments about the PVC gloves came from the supervisor at TF confirmed that the main area for failure was at the thumb web, and that the residual odour on the hands from the gloves discouraged workers from wearing them.

4.3.2 Nitrile-butadiene rubber gloves

There were two types of NBR gloves collected: Sol-Vex™ (Ansell Edmont) (n = 13) and the other manufactured by MSA Pty. Ltd.(n = 5). The MSA gloves did not have a trade name and are known as MSA™ hereafter. These gloves all came from the TF group and therefore were analysed by type. Failures found on the NBR gloves were cracks, macropores and punctures. The intact gloves were also compared by type. Only the counts of the macropores in the Sol-Vex™ gloves and the punctures in the MSA™ gloves passed the normality test. There were no differences in failures between the types. Cracks, T = 55.5, P = 0.454; macropores, T = 45.0, P = 0.840, punctures T = 45.0, P = 0.840. There was no difference in the proportion of intact gloves between the types (T = 47.0, P = 1.000).

The age of the NBR gloves was unknown, but all had been washed in detergent and water and stored in the light. A comment received from the supervisor about these

gloves was that they were not robust enough for farm work, tore easily and the main area of failure was at the thumb web.

There were four cracks (mean size 4 mm) in the NBR gloves, three were located at the thumb web and the other at the third and little finger interstice. There was only one macropore and this was located at the third and little finger interstice. There was only one puncture, which was on the palm.

4.3.3 Natural rubber gloves

There were two types of NR gloves collected from three origins. The gloves from the OR and TF origins were Hy-Care™ and the BG gloves were washing-up gloves. Cracks and splits were the only failures found on these gloves and their location and distributions are summarised in Table 4.6. There were no differences between origins for cracks ($H = 1.000$, d.f. = 2, $P = 0.890$. There were twelve splits found in the OR group and none in the TF and BG groups [mean = 3 ± 1.29 (se)]. However, the power of the performed test was low and the results need cautious interpretation ($F_{2,5} = 2.25$, $P = 0.201$).

TABLE 4.6

Location and distribution of failures in farmers' NR gloves. The codes are: T = thumb; F 1 = index finger; F 2 = middle finger; F 4 = little finger; TT 1 = thumb tip; FT 1 = index fingertip; A 1 = thumb web; and P = palm.

Failures	Number of failures	Distribution and location	Mean size (mm)
Cracks	2	1 F1, 1 P	0.2
Splits	12	2 F1, 1 F2, 2 F4, 4 T, 1 TT1, 1 FT1	13.0

All the NR gloves were one year old. BG 5–6 had been washed in detergent and water and stored in the dark. OR 7–8 had been washed in water and stored in the dark. OR 19–20 had not been washed and were stored in the light. Comments received on all the Hy-Care™ gloves were that they had been chosen for fit, comfort, grip function and tactility.

4.3.4 Thin polyvinyl chloride gloves

There were only three of these gloves collected, two of which were intact and the remaining one had a 5 mm crack located at the middle and third finger interstice. Therefore these gloves did not warrant statistical analysis. They were unwashed and

were heavily soiled, of unknown age and the farmer did not reply to the storage question.

4.3.5 Polyvinyl chloride/nitrile-butadiene rubber gloves

There were only two of these gloves collected. One was intact and the other had a 3 mm split located at the index and middle finger interstice. These gloves were five years old, discoloured yellow, had never been washed and were stored in the light in the tractor cab. The comments about these gloves were that "they are the best gloves I have ever owned" and that the discolouration was due to Stomp®.

4.3.6 Cotton/leather and leather gloves

The cotton/leather gloves had leather palms and fingers with cotton backs. Both of these gloves came from the OR group. Splits were the only failure and there was no difference between the types ($t = 1.11$, d.f. = 4, $P = 0.3288$). The incidence of the splits in the leather gloves had a mean of 2.25 ± 0.63 (se) and in the cotton/leather gloves the mean was 1 ± 1 (se). The power of the performed test was low and therefore invites cautious interpretation. The maintenance factors for the cotton/leather and leather gloves are detailed in Table 4.7. The leather glove (OR 20) had the third finger cut off and taped up with electrical insulation tape. Comments about these gloves were that they were used for chemical application and other purposes.

TABLE 4.7

Location and distribution of failures in farmers' cotton/leather and leather gloves. The codes are: T = thumb; F 3 = third finger; FT 1 = index fingertip; FT 2 = middle fingertip; F T3 = third fingertip; and FT 4 = little fingertip.

Splits	Number of splits	Location and distribution	Mean size (mm)
Leather	9	1 F3, 1 FT1, 3 FT2, 3 FT3, 1 T	4
Cotton/leather	2	1 FT4, 1 T	40

4.3.7 Pesticides used

A variety of pesticides were used within the different agricultural regions. The pesticides that were used with the collected CPGs are detailed in Table 4.8.

TABLE 4.8

Pesticides used by farmers from different agricultural enterprises. TF = Tahune Fields (mixed horticulture) OR = apple orchardists, DP = Derwent Park (sheep grazing), V = vegetable growers, BG = Botanical Gardens (ornamental horticulture).

Origin	Pesticide class	Pesticide trade name	Active ingredient
TF	Insecticides	Bugmaster	Carbaryl
		Carbaryl 800 WP	Carbaryl
		Chlorpyrifos 500 EC	Chlorpyrifos
		Folimat 800	Omethoate
		Gusathion 350	Azinphos-methyl
		Insegar 250 W	Fenoxycarb (insect growth regulator)
		Lorsban	Chlorpyrifos
		Thiodan EC	Endosulphan
	Fungicides	Aliette	Fosetyl
		Benlate	Benomyl
		Delan WP	Dithianon
		Dithane	Mancozeb
		Fulasin	Ziram
		Kocide	Copper
		Rimodil	Metalaxyl
		Rovral Aquaflow	Iprodione
		Thiram	Thiram
		Topas	Penconazole
	Herbicides	Asulox	Asulam
		Basta	Glufosinate-ammonium
		Cultar	Paclobutrazol
		Cytolin	Gibberellic Acid (growth regulant)
		Diuron 900	Diuron (D urea substitute)
		Ethrel	Ethephon (growth regulator)
		Flowable Gesatop	Simazine 250g/L Atrazine 250g/L
		Fusilade	Fluazifop
		Goal CT	Oxyfluorofen
		Lontrel	Clopyralid
		NAA	NAA
		Ramrod	Propachlor
		Round Up CT	Glyphosate
		Sprayseed	Paraquat 125g/L Diquat 75g/L
		Stomp 330 E	Pendmethalin
		Surflan	Oryzalin
		TL- Plus	Amitrol
DP 1–2	Herbicides	Grazon	Tryclopyr, butoxy
DP 3–4	Insecticides	Le Mat	Omethoate
	Herbicides	2,4-D	2,4-D
DP 5–6	Insecticides	Top Clip Blue Shield	Diazinon
	Herbicides	"Herbicides"	

Origin	Pesticide class	Pesticide trade name	Active ingredient
DP 7–8	Herbicides	"Herbicides"	
DP 9–10	Insecticides	Top Clip Blue Shield	Diazinon
	Herbicides	2,4-D	2,4-D
		Glyphosate	Glufosinate-ammonium
		Grazon	Triclopyr, butoxy
OR 1–6	"Orchard Chemicals"		
OR 7–8	Herbicides	Glyphosate	Glufosinate-ammonium
OR 9–10	Insecticides	Carbaryl	Carbaryl
		Gusathion	Azinphos-methyl
		Lorsban	Chlorpyrifos
		Thiodan	Endosulphan
	Fungicides	Baycor and Agridex	Bitertanol; Agridex is a non ionic wetting agent
		Bayleton	Triadimefon
		Delan	Dithianon
		Kocide	Copper
		Sulphur	Sulphur
		Systhane	Myclobutanil
		Thiram	Thiram
OR 11–12	Insecticides	Carbaryl	Carbaryl
		Gusathion	Azinphos-methyl
		Lannate	Methomyl
		Lorsban	Chlorpyrifos
		Pyrinex	Chlorpyrifos
		Thiodan	Endosulphan
	Fungicides	Baycor and Agridex	Bitertanol; Agridex is a non ionic wetting agent
		Delan	Dithianon
		Manzate	Mancozeb
		Nimrod	Bupiramate
		Nuster	Flusilazole
		Sulphur	Sulphur
		Thiram	Thiram
	Miscellaneous	Limil	Lime
		Urea	Urea
OR 13–14	Insecticides	Lorsban	Chlorpyrifos
		Thiodan	Endosulphan
	Fungicides	Bravo	Chlorothalonil
		Copper	Copper
	Herbicides	Mecopropamine	Mecoprop
*One item illegible on the returned questionnaire			
OR 15–20	Insecticides	Lorsban	Chlorpyrifos
		Thiodan	Endosulphan
	Fungicides	Bravo	Chlorothalonil
		Copper	Copper
	Herbicides	Linuron	Linuron
		Mecopropamine	Mecoprop
OR 20–26	"Insecticides" "Fungicides" "Herbicides"		

Origin	Pesticide class	Pesticide trade name	Active ingredient
BG 1–6	Insecticides	Hallmark	Esfenvalerate
	Fungicides	Bravo	Chlorothalonil
		Mancozeb	Mancozeb
		Rovral	Iprodione
	Herbicides	Glyphosate	Glufosinate-ammonium
V 1–2	Herbicides	Asulox	Asulam
		Banvel	Dicamba
		Brush Off	Metsulfuron
		Hoegrass	Diclofop
		Lexone	Metribuzin
		Linuron	Linuron
		MCPA	MCPA
		Reglone	Diquat
		Round-Up CT	Glyphosate
		Stomp	Penimethalin
		Tigrex	MCPA iso-octyl diflufenican
	Fungicides	Score	Difenoconazole

4.4 Discussion

Overall the exchange rate was poorer than anticipated given the extensive publicity about the project. One of the problems may have been that farmers did not hear about the project until they entered the rural retail outlets and of course did not have their old CPGs with them and may not have been returning to town for months.

Polyvinyl chloride gloves dominated the exchange program, as anticipated. Unexpectedly NBR gloves, which are well marketed as CPGs, only came from the TF group, which is undoubtedly due to their double gloving policy. Their thinness may be perceived by farmers as too delicate for typical farm use. It was somewhat surprising to receive NR, cotton/leather and leather gloves as they cannot be classified as CPGs. The NR gloves are not sold in rural retail outlets but are sold in the cleaning divisions of the safety shops and in some supermarkets. It may be that the NR gloves are perceived to be effective against water permeation and penetration and this may be extrapolated by some farmers to include all liquids. The leather/cotton and leather gloves are sold in the rural retail outlets as general purpose gloves for their physical barrier properties, but not as CPGs.

4.4.1 Polyvinyl chloride

The type of farming practice did not have any influence upon the type or number of failures found in the group of PVC gloves. Polyvinyl chloride gloves were typically washed in water and detergent and stored in the light. This was difficult to interpret as

there are no guidelines or protocols in Tasmania for cleaning and storage of gloves and certainly no information is provided on the glove labels or packaging nor on the pesticide container labels. It can be assumed that farmers generally treat their PVC gloves in the same manner as their other protective clothing.

The mean age of the PVC gloves was two years and this could imply their usage over two spraying and/or dipping seasons.

Macropores represented the most common type of failure in the PVC gloves although it is rather misleading to generalise as most of the macropores occurred on a single glove at the third little finger interstice. Macropores are related to the manufacturing process and cannot technically be regarded as a failure, but their presence may considerably weaken the glove structure and the decrease in thickness may enhance permeation of pesticides.

Splits predominantly occurred at the interstices, particularly the middle and third finger interstice and the third and little finger interstice. Cracks occurred mainly at the third and little finger interstice followed by the thumb web. This may be because of the straightness (*i.e.* not contoured) of the fingers in the Chinese gloves, which would not allow for much give, *e.g.* in a grasping situation. Cracks may develop into splits and may harbour pesticide residues and the decrease in thickness will enhance permeation. Punctures mainly occurred at the thumb interstice, and probably were the results of grasping situations. The main problem with splits and punctures is that penetration of chemicals can more readily occur. These results also support the finding of Bromwich *et al.* (1994–1995, pp.70–71), although they did not elaborate on the type of failure other than to mention that they were mechanical in nature.

The relatively high number of splits and punctures was unforeseen. Splits and punctures are clearly visible failures (the means were 6 mm and 10 mm respectively) and therefore it could be assumed that these gloves should have been retired. This indicates that farmers do not regularly check their gloves for failures.

Considering the undesirable storage of DP 1–8 it was expected that there would be some damage from friction. However, this was not the case.

4.4.2 Nitrile-butadiene rubber

These gloves were in relatively good condition, with few failures and no differences between types. Cracks were located on the thumb web, which support the supervisors claim that this is the most frequent site for failures.

4.4.3 Natural rubber

Splits were the most common form of failure for these types of gloves. There were insufficient data to make firm conclusions, but there was no difference between types. Again it was surprising that these gloves were still in use given the large size of the splits (mean = 13 mm).

The interesting comment concerning all the Hy-Care™ gloves was their superior fit. These gloves are nicely curved to meet a normal hand shape. The hand form of the Chinese gloves has straighter fingers and a flatter body making them more cumbersome with a resultant loss of dexterity, grip function, tactility and comfort. The maintenance data were variable. However, as there were no significant differences in the failures between the groups no conclusions could be drawn.

4.4.4 Thin polyvinyl chloride

These gloves could not be identified as to the manufacturer and were only classified as thin PVC (Chapter Six). They were not sold as CPGs and as the farmer did not complete the questionnaire their working history is unknown. Although they only had one crack they did not appear robust enough for general farm work.

4.4.5 Polyvinyl chloride/nitrile-butadiene rubber

Considering the age of these gloves and their poor maintenance they were in remarkably good condition. It is unfortunate that there were not more of these gloves collected.

4.4.6 Cotton/leather and leather

It was not anticipated that cotton/leather and leather gloves would be involved in the exchange program. It should be evident that these gloves should not be used for pesticide application as they are not even effective barriers against water, would change colour when wet and the epidermis would become easily exposed. These gloves were used for other purposes and these issues suggest that the owner was not well educated in pesticide handling and safety.

4.5 Chapter Summary And Conclusions

This research which has been completed with the cooperation of many retailers and farmers, has provided for the first time important information about what types of gloves farmers are wearing when applying pesticides in Australia. Prior to this research, knowledge of CPGs used by farmers was based on anecdotal evidence from individual farmers and selected retailers. Polyvinyl chloride gloves made in China dominate the market. They have many inclusions and their quality is not uniform.

Farmers typically use their CPGs for two seasons of pesticide application. Given the number of visible failures reported here this is too long and they should be discarded after one season.

Farmers use and treat their gloves in a haphazard manner. Fewer than half of the returned gloves were intact and it is evident that guidelines need to be introduced to encourage farmers to visually examine their gloves before they are put into use. There was no uniformity in the maintenance of gloves. More research should be directed to this area, which would result in guidelines and protocols with the aim of improving farmer safety.

Some gloves in use were inappropriate for pesticide application and appropriate information should be provided on the pesticide container labels, on the CPGs and in the rural retail outlets. The double gloving technique used at TF seems to be a good precautionary practice, although it was not known why workers did not comply with the protocols and this warrants further exploration.

The large diversity of pesticides in use suggests that research into individual chemical permeation profiles is not appropriate for evaluating CPGs used in agricultural work required to provide an effective barrier against many pesticides and other agents. It is not known if the CPGs that farmers wear have microscopic defects and this question is examined in detail in the next chapter.

Chapter Five

An Evaluation Of The Surface Topography Of Chemically Protective Gloves Following Their Use In Agriculture

5.1 Introduction

Visualisation of the surface topography of CPGs can yield valuable information about the integrity of the material and therefore its likely efficiency. The structures of polymers have been observed by both light and electron microscopy. Scanning electron microscopy (SEM) on uncoated specimens has been the usual means of observation (Henry 1986; Moody and Nadeau 1992).

The main advantages of using SEM methods over optical microscopy are that higher resolutions and a much greater depth of field can be achieved. The major limitation of SEM is that often non-conductive materials require coatings of conductive materials for microscopy and this applies to most polymers. At very high magnification the application of such coatings can give rise to several artefacts, *e.g.* in the form of grain structures from the coating.

The advantage of using an environmental scanning electron microscope (ESEM) instead of a SEM is that it operates in a low vacuum and the specimen does not require coating and therefore there is a more realistic image of the surface structures.

Ubiquitous problems that are general to both SEM and ESEM techniques are caused by primary irradiation effects on polymers, which can result in ionisation and rupture of chemical bonds. Secondary effects include chain scission or cross linking, generation of heat, reversible charging and mass loss (Michler 1993). Other artefacts can be caused by the substance that is used to affix the specimen to the stub as it may wick up and contaminate the surface (Sawyer and Grubb 1987, p.274). However, this can be almost totally avoided by selecting the right observation conditions, accelerating voltage and beam and by use of suitable adhesives.

There have been only a few microscopic examinations of CPGs and usually for illustrative purposes only, rather than analysis. Moody and Nadeau (1992) used a JEOL JSM-6400 SEM to examine uncoated NR gloves before and after treatment with DEET and following UV-A exposure for up to four days. The operating conditions were not detailed. They reported that there was no difference between the UV-A exposed and unexposed specimens at 500 x, although microchannels were present in the unexposed specimen. However, at 10,000 x there was a greater number of microholes visible, 0.1–0.2 μm in diameter. In specimens treated with DEET for twenty-four hours in the dark, the surface structure was altered so that the microchannels disappeared and the surface had a molten appearance at 1000 x because of the possible absorption of DEET (Jablonski *et al.* 1982). These observations are somewhat difficult to interpret as they have not been done at comparative

magnifications. It also seems odd that they did not report any damage from the electron beam and this may have been a contributing factor to the molten appearance.

In a study that examined the permeation of epichlorohydrin, perchlorethylene, trichloroethylene and 1,2-dibromoethane through several types CPC materials it was reported that Teflon™ specimens produced inconsistent results (Stampfer *et al.* 1984). One explanation given was that the specimens were thoroughly flexed before they were placed in the ASTM cell and this caused some superficial surface ruptures, which may have led to the differing permeation profiles. This rupturing is evident on the electron micrograph, but because there were no micrographs taken of unflexed specimens this explanation can only be tentative. Small holes were noted on an electron micrograph of PVA that had been soaked in water for four hours, but again there were no comparative untreated PVA micrographs (Stampfer *et al.* 1984).

Exposure to chlorine gas caused brittleness in neoprene specimens without permeation occurring. At 100 x, by electron microscopy, it was found that the exposed specimens had raised cracks with "irregularly shaped linear platelike structures" (Henry 1986, pp.53–54).

In work related to the aims of this thesis, the surface topography of NBR and PVC gloves that had been exposed to three OPs (Top Clip Blue Shield®, a sheep dipping agent a.i. diazinon; Malathion® a.i. maldison; and Lorsban ® a.i. chlorpyrifos) in conjunction with outdoor environmental factors was assessed by the ESEM 2020 and gridded template method. This study found that the Top Clip Blue Shield® was the most aggressive chemical on the PVC gloves, and that both types of gloves cracked following chemical exposure (Canning 1995).

The aims of this study were:

1. to develop a taxonomy of defects for CPGs;
2. to determine the types of defects that occur in new and used CPGs for agricultural use;
3. to compare different types of CPGs within this classification system;
4. to determine if storage, maintenance and age are factors that influence the frequency and types of defects in used gloves; and
5. to determine the physical effects of short and medium term exposure to concentrated and diluted OPs, as may occur with a splash or spill.

5.2 Materials And Methods

5.2.1 Comparison of new and used gloves

The gloves were the same ones described in Chapter Four (4.3) but with the addition of new gloves purchased from MSA Australia Pty. Ltd. and Eastside Agencies Pty. Ltd., Hobart, Tasmania. The cotton/leather and leather gloves were not included in this section because they did not meet the criteria for impervious gloves or CPGs.

The gloves were sectioned down the side seams with sharp scissors and specimens measuring 3 cm x 3 cm were cut from the palm section of the gloves 2 cm in from the thumb junction. The specimens were then sampled haphazardly with an in-house designed aluminium punch, which gave 6 mm diameter samples. One sample from each specimen was used in the analyses. These samples were affixed to aluminium stubs with clear fast drying nail polish. At all times great care was taken so that there was never any contact with the surface of the sample. The samples were transferred to the stubs with forceps, and afterwards the mounted stubs were always transferred with forceps. The mounted samples were kept in specially prepared boxes and stored in a refrigerator at 4°C to maintain a constant environment until analysed.

5.2.2 Immersion experiments

Three different immersion experiments were conducted: 1) the external surfaces were exposed for three different time intervals to two different formulated OPs; 2) the external surfaces were exposed for one minute to the same OPs as in 1); and 3) both surfaces of the materials were exposed to one formulated OP for the same time intervals.

5.2.2.1 Immersion of external surfaces

These experiments were conducted to determine the effects of exposure to the external surface of PVC and Sol-Vex™ gloves to OPs. Matching fingers were cut from PVC and Sol-Vex™ gloves from the same batches and checked for visible defects. Three 50 mL beakers were filled up to 2 cm from the top with concentrated Jetdip® (Virbac, a sheep dip, jetting fluid and blow fly dressing, a.i. diazinon 200g/L with 522g/L liquid hydrocarbon, Batch 11762v1, expiry date August 1998, purchased from Websters Pty, Ltd. Hobart, Tasmania) and another three with diluted Jetdip®. The diluent was water and it was diluted to give diazinon 0.1 gm/L, for dipping. The same procedure was repeated using Lorsban 500 EC® (Dow Elanco Australia Ltd. insecticide, a.i. chlorpyrifos 500g/L with 491 g/L liquid hydrocarbon, date of manufacture February 1995, Batch 950204–01 dilution at 50 mL/100L purchased from Roberts Pty. Ltd., Huonville, Tasmania). (Lorsban 500 EC® is referred to as

Lorsban® from now on.) Lorsban® was diluted to give chlorpyrifos 0.25 g/L, for wingless grasshoppers. The finger tops were threaded with wire and attached to labelled pegs, which in-turn were supported by wire. Each glove finger, with its attachments, was placed in its appropriate labelled beaker. Approximately 1–2 cm of the proximal section of the glove finger remained above the level of the OPs and could not be totally submerged. These were kept *in situ* for twenty-four, thirty-six and forty-eight hours. After the time had elapsed the specimens were removed with forceps and the external surfaces were gently squirted with 50 mL of distilled water. Then they were suspended in a clean 1 L beaker with 50 mL of distilled water and agitated manually for one minute so that only the external surfaces received cleaning treatment. The last procedure was repeated three times in total.

The sample preparation technique was the same, although the samples were taken from the distal portion of the finger near the tip but avoiding the seamed section. The PVC immersed in the concentrated Lorsban® for thirty-six and forty-eight hours had permeated or penetrated through to the lining of the glove fingers, which were visibly moist. To eliminate the possibility of condensation forming on the interior surface four more fingers were subjected to these immersion times. However, the tops of the glove fingers were securely fastened together with electrical tape. Untreated fingers from the same batches were used as controls. The ESEM observations of the surface of new Sol-Vex™ glove fingers revealed that the surface topography was non-uniform and therefore comparisons were not beneficial. Consequently this part of the experiment was repeated using the whole glove, with 1 L beakers, and sampling from the non-textured palm section as happened in the new and used NBR gloves.

5.2.2.2 One minute immersion

Two pairs of matching fingers from PVC gloves, from the same batch as the finger immersion experiments, were immersed for one minute in concentrated Jetdip® and Lorsban®. The same was repeated with the whole Sol-Vex™ gloves. These gloves were not cleansed and allowed to drip dry in the fume hood for twenty four-hours. The fan was left off to minimise air movement thus decreasing particulate motion. The sampling technique was the same as previously described.

5.2.2.3 Immersion of both surfaces

This experiment involved immersion of specimens of new NBR (Sol-Vex™) and PVC gloves in neat Top Clip Blue Shield® (Ciba-Geigy Australia, a sheep dip, jetting fluid and blow fly dressing, a.i. diazinon 200g/L with 522g/L liquid hydrocarbon, Batch 1033860, date of manufacture September 1993, purchased from Websters Pty, Ltd. Hobart, Tasmania). The specimens were obtained as described above. Four

specimens of each type of glove were placed in 50 mL beakers and covered with Top Clip Blue Shield®. After twenty-four hours two specimens were removed with forceps, both sides gently squirted with 50 mL of distilled water, put in a clean 1 L beaker with 50 mL of distilled water and agitated manually for one minute. The last procedure was repeated three times in total. The remaining two specimens received no cleaning treatment. The specimens were attached to labelled pegs and suspended in a fume hood and allowed to air dry for thirty-six hours. This process was repeated for both types of glove specimens following thirty-six and forty-eight hours immersion in Top Clip Blue Shield®. When the specimens were dry they were treated in the same manner as the used gloves. Samples were prepared from new gloves that were from the same batches as those which were immersed.

5.2.3 Electron microscopy

An ESEM 2020 was used to observe the physical defects of the surface. Operating conditions ranged from 15–20 accelerating voltage (kV) and specimen chamber pressure of 3.5–4.2 Torr (T) with water vapour as an active medium. Initially each sample was examined at low magnification (80–100 x) to assess the overall surface topography. The magnification was then increased to 400 x, the contrast and brightness controls were adjusted via the oscilloscope and the scan time was increased to .48 seconds from .12 seconds and the image was focussed. The surface topography was re-examined at this magnification and when a representative image was selected the magnification was increased to 500 x in the scan mode and the focus, brightness and contrast were readjusted. The magnification was reduced to 400 x, the scan mode turned off and then an acquisition was made. The contrast and brightness of the acquired image were readjusted, if necessary, for optimum visualisation and then a micrograph was taken. One micrograph was taken per sample at 400 x, and in some cases higher or lower magnification was used additionally to illustrate the entire surface structure or an interesting feature. Ilford FP4 (125) films were used and were developed and prints made of the micrographs by the University Photographic Services.

In the immersion experiments it was sometimes difficult to obtain a sharp focus because a film had formed over the surface of the gloves by the residual OPs. In these circumstances two micrographs were taken of the same region; one with comparable operating conditions and for the other, the accelerating voltage was increased to 20 kV in order to enhance visualisation of the sub-surface structures more readily.

The other method used was to broadly scan the surface at 400 x and make at least four acquisitions to ensure that the image was representative of the sample. However, this

method was performed less often as the candidate became more adept at using the instrument.

5.2.4 Scoring the data

A taxonomy of surface defects was developed and included: cracks; cavities; convexities; smooth areas; slumps; contaminants; and crazed areas (Table 5.1; Figure 5.1). Figure 5.2 shows comparisons of the surface topography of new and used gloves.

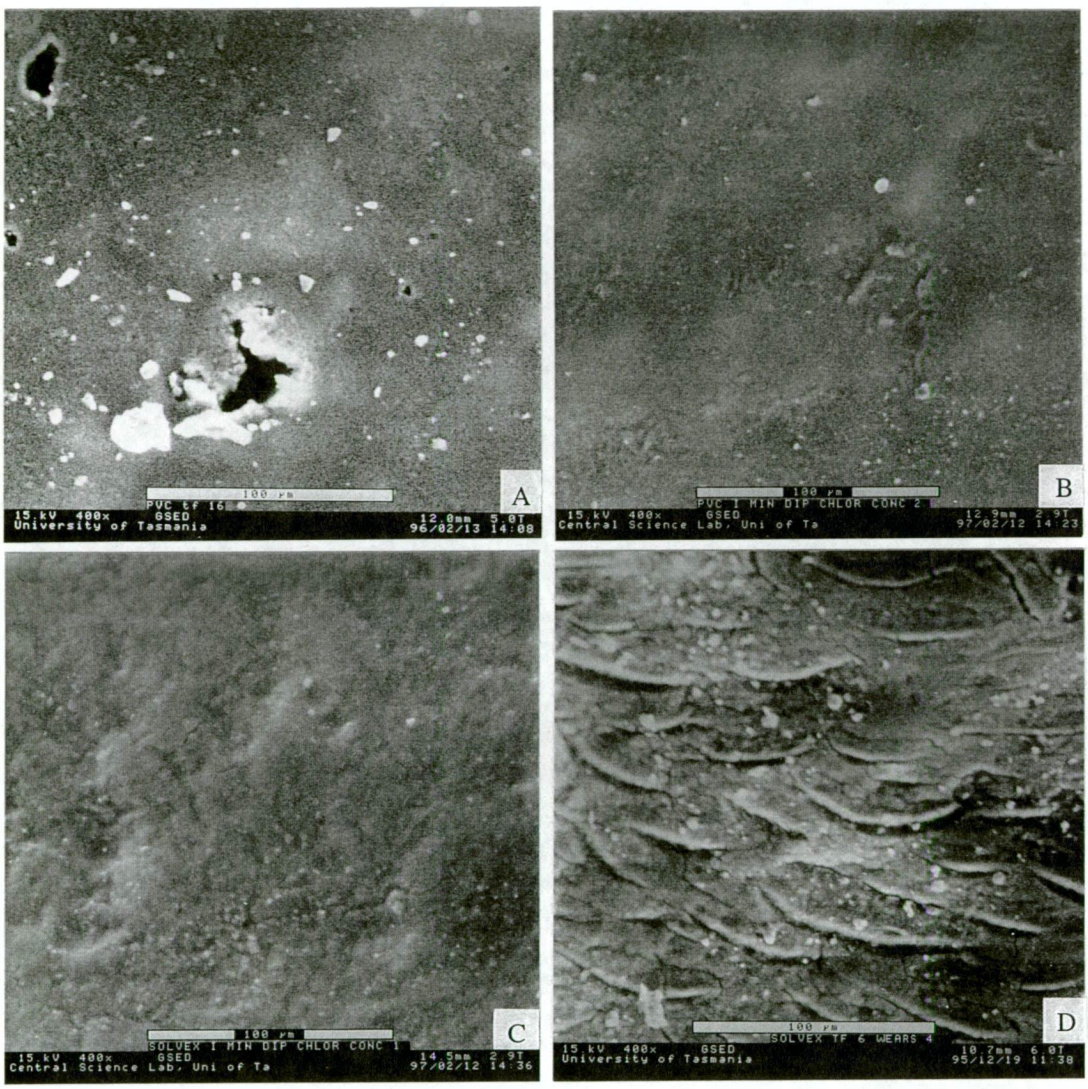
TABLE 5.1

Taxonomy of the surface defects of chemically protective gloves at a magnification of 400 x

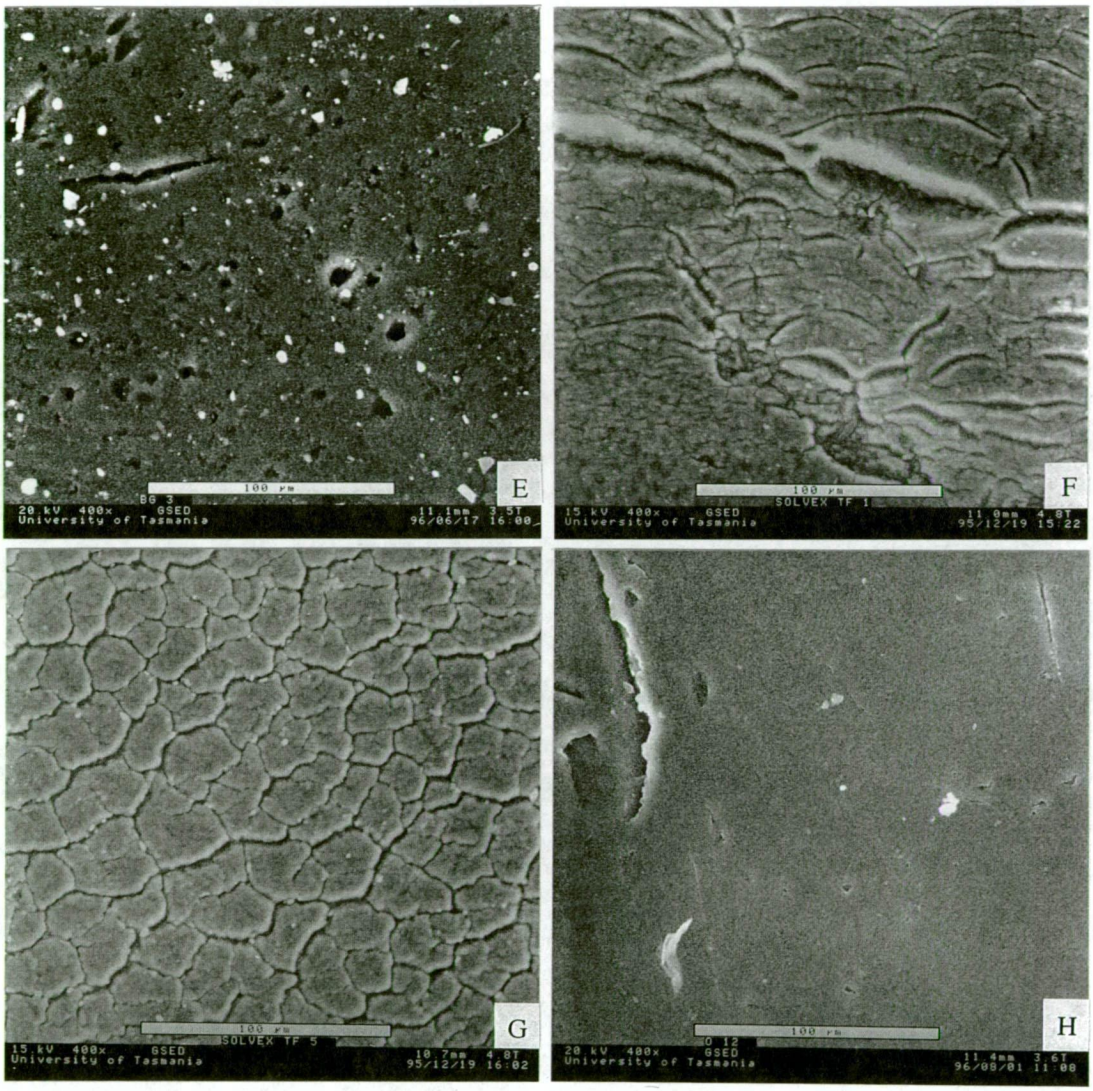
Surface defects	Description
Cavities	Concave forms such as holes, bubbles, pores and sink marks which may be regular or irregular in shape
Contaminants	Various substances not integral to the glove structure
Convexities	Lumps and bumps which may be regular or irregular in shape
Cracks	Parting of the surface structure and the formation of new surfaces
Crazes	Very fine cracks usually forming enmeshed interconnected patterns
Slumps	Regular rolled semi-circular raised areas
Smooth areas	An absolute value was given for this (either it was smooth or it was not)

FIGURE 5.1

Environmental scanning electron micrographs (400 x) showing the surface defects on PVC and NBR gloves



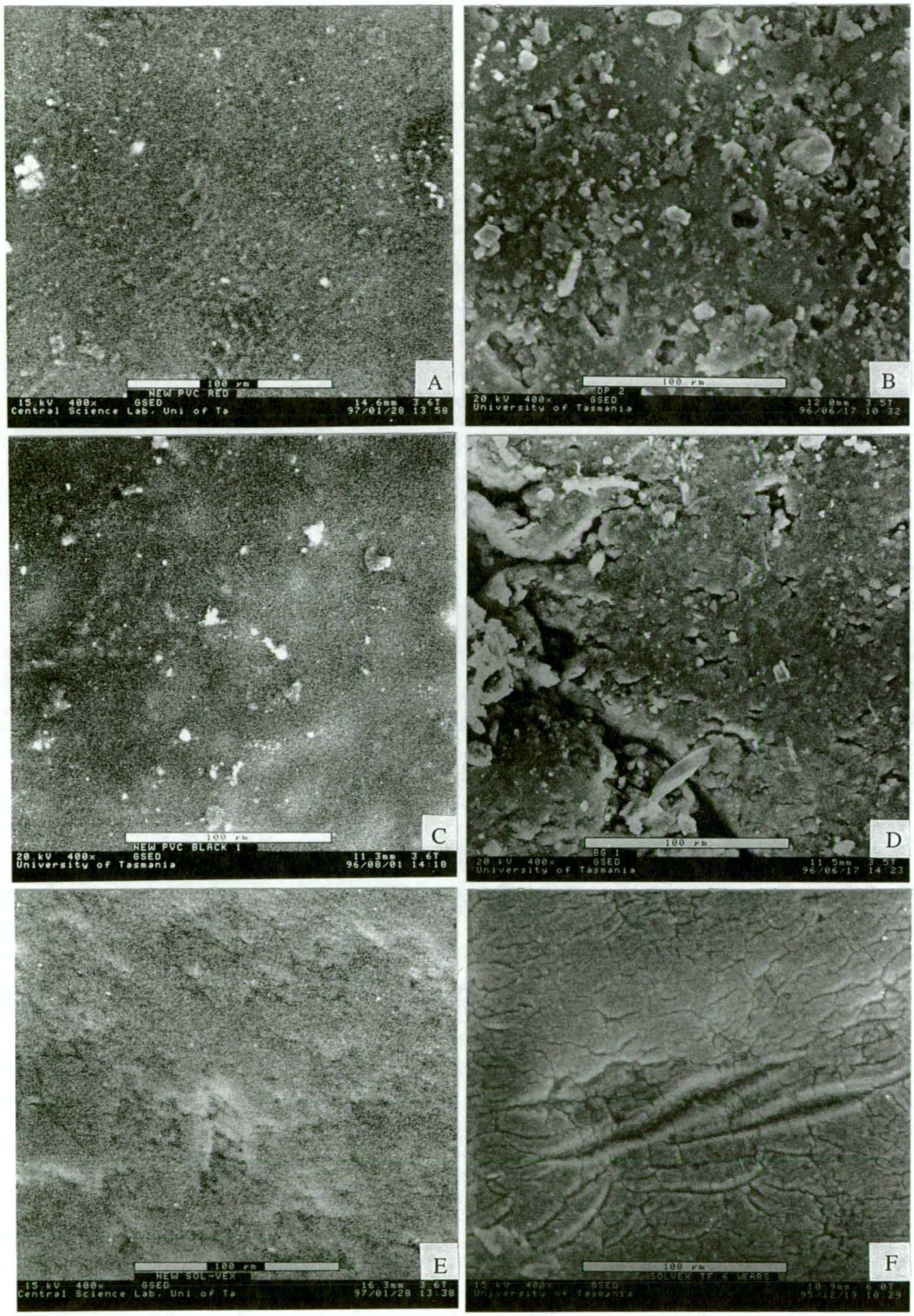
A: Cavities and contaminants on PVC
B: Convexities on PVC
C: Convexities and contaminants on Sol-Vex™
D: Slumps and contaminants on Sol-Vex™



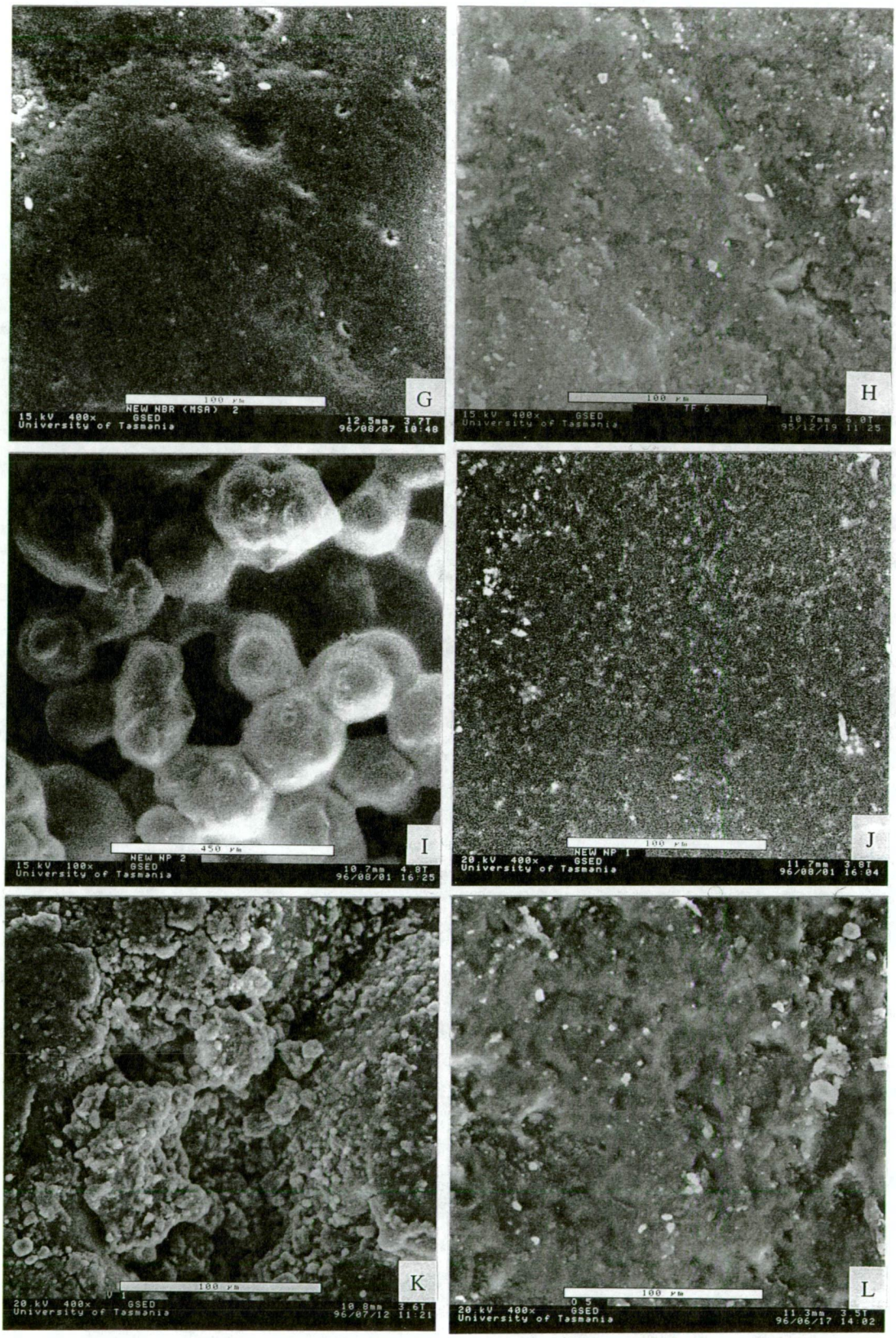
E: Cracks, cavities and contaminants on PVC
F: Cracks and cavities on Sol-Vex™
G: Crazing on Sol-Vex™
H: Smooth areas on PVC

FIGURE 5.2

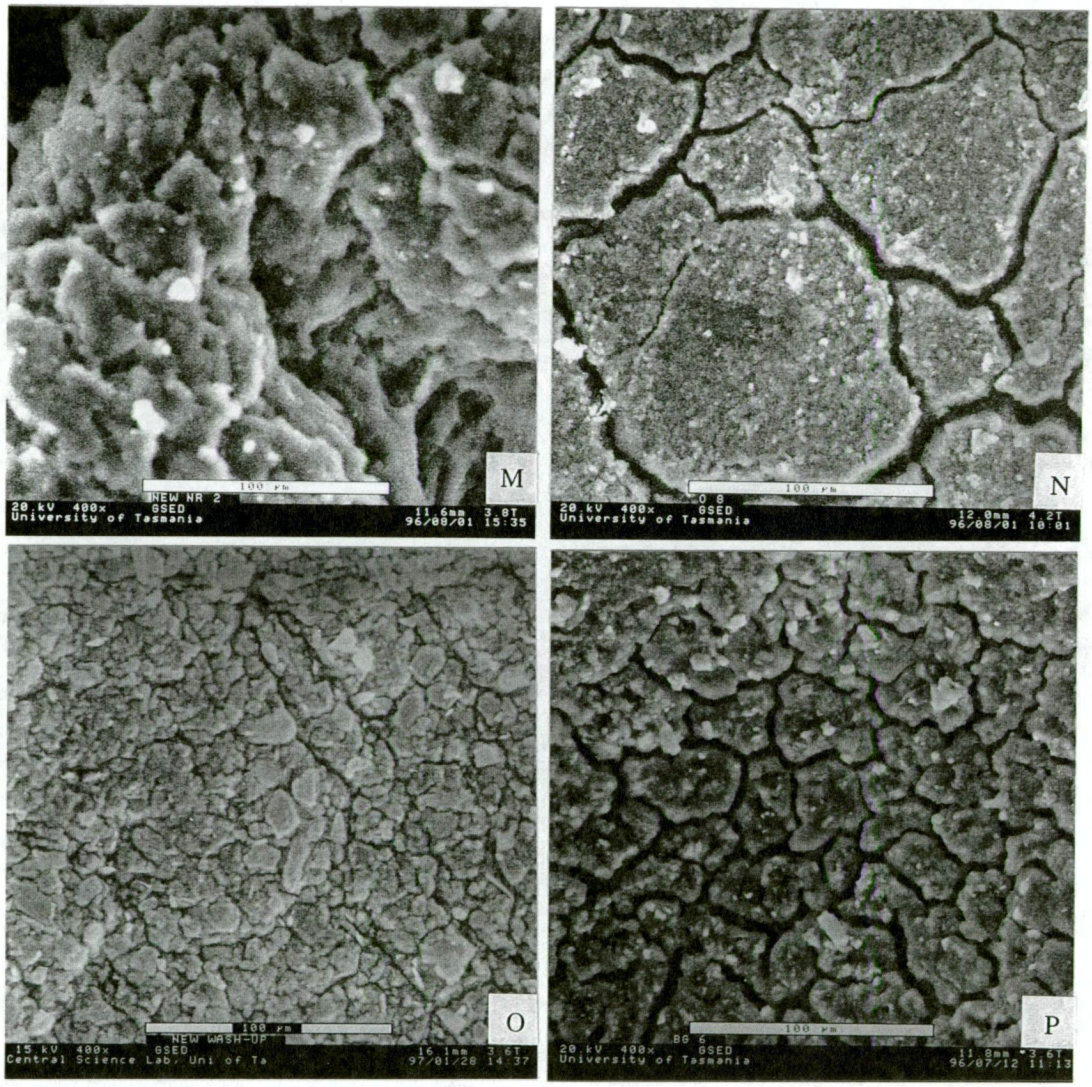
Comparison of the surface topography (400 x) of new and used gloves from the exchange program



A: New red PVC. B: Used red PVC, showing cavities and contaminants.
C: New black PVC, showing convexities and contaminants. D: Used black PVC showing, cracks, cavities and contaminants.
E: New Sol-Vex™, showing cavities. F: Used Sol-Vex™, showing cracks.



G: New MSA™ showing convexities and cavities. H: Used MSA™, showing cavities and contaminants. I and J: New PVC/NBR, showing great variation in the surface topography. K: Used PVC/NBR, showing cavities and contaminants. L: Thin PVC.



M: New Hy-Care™, showing cavities, convexities and contaminants. N: Used Hy-Care™, showing cracks and contaminants. O: New washing-up gloves, showing convexities and contaminants. P: Used washing-up gloves, showing cracks, cavities, convexities and contaminants.

Initially the contact images were scanned (Hewlett Packard Company Scan Jet 4C Microsoft Windows Version 1995 and imported into Sigmascan/image™ measurement software (Jandel Scientific 1994). Defects on the images were counted and measured both in the linear mode and in the perimeter mode, after which the areas were calculated. This technique was fraught with logistical problems. Many of the defects lacked distinct boundaries, which made actual measurements difficult to digitise. This also made it virtually impossible for two or more people to obtain the same results, causing a problem with reliability. It was also rather cumbersome and time consuming as a new image had to be imported for each defect. This method was found to be ineffective and abandoned.

A new method that involved counts of defects rather than area measurements was found to be valid and reliable. A gridded template was made on a transparent overlay to give twenty rectangles measuring 14 mm x 10 mm. All the rectangles were numerically coded and ten random numbers were generated on a scientific calculator (Casio Super-Fx) and those ten nominated were coloured in black. The overlay was placed over the micrograph contact prints, which left ten transparent rectangles. These were coded thus allowing for 50% of the surface to be viewed. Recording charts were designed, which contained the glove code, the grid code and all the defects. Every defect observed through the transparent grid rectangles was recorded in its allocated cell.

5.2.5 Statistical analyses

Counts of defects were not normally distributed (Kolmogorov-Smirnov Test) nor were variances equal (Levene Median Test). Transformation of the counts failed to adequately normalise most of them. Consequently the influence of glove material on each class of surface defect was investigated with Kruskal-Wallis one way ANOVA on Ranks using the statistical program SigmaStat™ (Jandel Scientific Software 1994). The results of all pairwise multiple comparison tests were determined with Dunn's Test since the sample sizes were unequal. The analyses of the immersion experiments were similar, but because the sample sizes were equal the all pairwise multiple comparison tests were conducted using the Student-Newman-Keuls method. A few data sets were normally distributed and a One Way ANOVA was conducted when appropriate. The data for the one minute immersion experiments were analysed with Mann-Whitney Rank Sum Tests.

5.3 Results

The results of the used gloves from the exchange program are described under their polymer or elastomer group headings. The results of the immersion experiments are segregated by their glove type, PVC followed by NBR.

5.3.1 Gloves in field use

5.3.1.1 Polyvinyl chloride gloves

Defects in PVC gloves of various agricultural enterprise origins are summarised in Tables 5.2 and 5.3. Initially the two types of PVC gloves were treated as separate groups. However, the differences were not significant and therefore they were combined.

There were one hundred and sixty-four cracks in the used PVC glove samples and none on the new PVC. The PVC gloves were distinctive because they did not exhibit slumps or crazing. Cracks in PVC differed with origin ($H = 24.6$, d.f. = 4, $P < 0.001$). There were fewer cavities in the new gloves and they differed with origin ($H = 127.4$, d.f. = 4, $P < 0.001$). Convexities on PVC gloves differed between origins ($H = 44.1$, d.f. = 4, $P < 0.001$), but there were fewer in used gloves. Contaminants on PVC gloves differed very strongly between the groups ($H = 117.6$, d.f. = 4, $P < 0.001$) and were least abundant on the new gloves. There were only seven cases of smooth areas in the aggregate samples and, this therefore, did not warrant further statistical consideration.

TABLE 5.2

Defects per unit area on the surface of PVC gloves from various farm origins. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Origin	n	Median	25%	75%
Cavities	TF	190	2	1	3
	OR	130	4	2	7
	DP	100	5	3	8
	BG	40	4	4	7
	New PVC	50	1	1	2
Contaminants	TF	190	8	5	12
	OR	130	7	4	10
	DP	100	6	3	9
	BG	40	4	2	6
	New PVC	50	1	0	2
Convexities	TF	190	1	0	3
	OR	130	0	0	2
	DP	100	2	0	4
	BG	40	0	0	0
	New PVC	50	2	1	3
Cracks*	TF	190	0	0	0
	OR	130	0	0	0
	DP	100	0	0	0
	BG	40	0	0	0
	New PVC	50	0	0	0

* The mean for cracks = 0.32

TABLE 5.3

Comparison of defects per unit area on the surface of PVC gloves from various farm origins (Dunn's method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		Origin				
		TF	OR	DP	BG	New
Cavities	TF					
	OR	<0.05				
	DP	<0.05	NS			
	BG	<0.05	NS	NS		
	New	NS	<0.05	<0.05	<0.05	
Contaminants	TF					
	OR	NS				
	DP	<0.05	NS			
	BG	<0.05	<0.05	NS		
	New	<0.05	<0.05	<0.05	<0.05	
Convexities	TF					
	OR	NS				
	DP	NS	<0.05			
	BG	<0.05	NS	<0.05		
	New	<0.05	<0.05	NS	<0.05	
Cracks	TF					
	OR	<0.05				
	DP	NS	NS			
	BG	NS	NS	NS		
	New	NS	<0.05	<0.05	NS	

5.3.1.2 Nitrile-butadiene rubber gloves

There were two types of NBR gloves collected, Sol-Vex™ and MSA™. As these gloves all came from the same origin they were categorised by type and the defects are summarised in Tables 5.4 and 5.5.

Cracks in the NBR gloves differed by type ($H = 25.6$, d.f. = 3, $P < 0.0001$), as did cavities ($H = 59.5$, d.f. = 3, $P < 0.0001$). Most cavities were in the used MSA™ and least in the Sol-Vex™. Contaminants were variable between groups ($H = 39.1$, d.f. = 3, $P < 0.0001$) and there were none on the new control gloves. There were very significant differences between groups for convexities ($H = 103.8$, d.f. = 3, $P < 0.0001$) and for crazes ($H = 118$, d.f. = 3, $P < 0.0001$). Crazes were evident on the used Sol-Vex™ gloves and there were more convexities in the new gloves. Slumps, which were exclusively a feature of NBR, varied between groups ($H = 18.4$, d.f. = 3, $P = 0.0004$).

TABLE 5.4

Defects per unit area on the surface of NBR gloves from two manufacturers. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Glove type	n	Median	25%	75%
Cavities	Sol-Vex™	110	0	0	1
	MSA™	50	3	1	6
	New MSA™	20	2	0	5
	New Sol-Vex™	20	1	0	3
Contaminants	Sol-Vex™	110	0	0	1
	MSA™	50	2	0	6
	New MSA™	20	0	0	0
	New Sol-Vex™	20	0	0	0
Convexities	Sol-Vex™	110	0	0	0
	MSA™	50	2	0	4
	New MSA™	20	2	1	2
	New Sol-Vex™	20	2	1	3
Cracks	Sol-Vex™	110	0	0	0
	MSA™	50	1	0	2
	New MSA™	20	1	0	3
	New Sol-Vex™	20	0	0	0
Crazes	Sol-Vex™	110	6	3	10
	MSA™	50	0	0	0
	New MSA™	20	0	0	0
	New Sol-Vex™	20	0	0	0
Slumps	Sol-Vex™	110	0	0	0
	MSA™	50	0	0	0
	New MSA™	20	0	0	0
	New Sol-Vex™	20	0	0	2

TABLE 5.5

Comparison of defects per unit area on the surface of new and used NBR gloves from two manufacturers (Dunn's method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		Glove types			
		Sol-Vex™	MSA™	New MSA™	New Sol-Vex™
Cavities	Sol-Vex™				
	MSA™	<0.05			
	New MSA™	<0.05	NS		
	New Sol-Vex™	NS	NS	NS	
Contaminants	Sol-Vex™				
	MSA™	<0.05			
	New MSA™	<0.05	<0.05		
	New Sol-Vex™	<0.05	<0.05	NS	
Convexities	Sol-Vex™				
	MSA™	<0.05			
	New MSA™	<0.05	NS		
	New Sol-Vex™	<0.05	NS	NS	
Cracks	Sol-Vex™				
	MSA™	NS			
	New MSA™	NS	NS		
	New Sol-Vex™	NS	<0.05	<0.05	
Crazes	Sol-Vex™				
	MSA™	NS			
	New MSA™	NS	NS		
	New Sol-Vex™	NS	NS	NS	
Slumps	Sol-Vex™				
	MSA™	NS			
	New MSA™	NS	NS		
	New Sol-Vex™	<0.05	<0.05	<0.05	

5.3.1.3 Natural rubber gloves

Two types of NR gloves were collected—a thinner type of unsupported washing-up glove, and the thicker type of cotton knit lined glove (Hy-Care™, Ansell Edmont). The washing-up gloves were in the BG group and in the new washing-up groups, all the others were Hy-Care™. The defects found on the NR gloves are presented in a condensed form in Tables 5.6 and 5.7.

There were no crazed areas, smooth areas or slumps on these gloves. Cracks varied between groups ($H = 82.4$, d.f. = 4, $P < 0.0001$). Cavities differed between groups ($H = 36.8$, d.f. = 4, $P < 0.0001$). There were differences between the groups for

convexities (H = 54.7, d.f. = 4, P <0.0001). There were also differences between the numbers of contaminants between the groups (H = 46.2, d.f. = 4, P <0.0001).

TABLE 5.6

Defects per unit area on the surface of two different types of NR gloves. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Origin	n	Median	25%	75%
Cavities	TF	20	7	4	10
	OR	40	2	0	4
	BG	20	6	4	11
	New washing up	20	7	6	10
	New NR	20	5	4	7
Contaminants	TF	20	8	3	13
	OR	40	0	0	2
	BG	20	1	0	3
	New washing up	20	0	0	0
	New NR	20	0	0	1
Convexities	TF	20	3	2	5
	OR	20	4	2	7
	BG	20	6	3	8
	New washing up	20	14	12	15
	New NR	20	6	4	7
Cracks	TF	20	0	0	0
	OR	20	3	2	5
	BG	20	1	0	4
	New washing up	20	0	0	0
	New NR	20	0	0	0

TABLE 5.7

Comparison of the number of defects per unit area on the surface of two types of new and used NR gloves from various origins. BG and New WU were washing-up gloves; the others were Hy-Care™ (Ansell Edmont) (Dunn's method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		Origin				
		TF	OR	BG	New WU	New NR
Cavities	TF					
	OR	<0.05				
	BG	NS	<0.05			
	New WU	NS	<0.05	NS		
	New NR	NS	<0.05	NS	NS	
Contaminants	TF					
	OR	<0.05				
	BG	<0.05	NS			
	New WU	<0.05	NS	<0.05		
	New NR	<0.05	NS	NS	NS	
Convexities	TF					
	OR	NS				
	BG	NS	NS			
	New WU	<0.05	<0.05	<0.05		
	New NR	NS	NS	NS	<0.05	
Cracks	TF					
	OR	<0.05				
	BG	<0.05	<0.05			
	New WU	NS	<0.05	<0.05		
	New NR	NS	<0.05	<0.05	NS	

5.3.1.4 Polyvinyl chloride/nitrile-butadiene rubber gloves

Only one pair of PVC/NBR gloves was collected. The surface of these gloves was not uniform (Figure 5.2) and consequently the data were not aggregated. Two additional samples (V3 and V4) were taken from the same locations but on the dorsal side. V3 is the dorsal sample from V1, and V4 is the dorsal sample from V2. In total there were only twelve cracks in these samples and of these there were none in the new samples or in V4, nine were from the palmar surfaces and only three from V3. However, the differences in the median values were not great enough to be statistically significant ($H = 8.15$, d.f. = 5, $P = 0.1480$).

Cavities passed the normality test but failed the equal variance test. There were differences between the groups ($H = 33.9$, d.f. = 5, $P < 0.0001$). When these results were checked with Bonferroni's multiple comparison method the results were dissimilar, but in the interests of consistency it was decided to present the results from

Dunn's method. Convexities differed by group ($H = 26.8$, d.f. = 5, $P < 0.0001$). Smooth areas were only found on the New 2 sample and the difference was significant ($H = 5.5$, d.f. = 5, $P = 0.00834$). Contaminants also contrasted by group ($H = 23.0$, d.f. = 5, $P = 0.0003$). A summary of the defects is presented in Tables 5.8 and 5.9.

TABLE 5.8

Defects per unit area on the surface of new and used PVC/NBR gloves. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Origin	n	Median	25%	75%
Cavities	V1	10	6	3	7
	V2	10	4	2	4
	V3	10	8	6	12
	V4	10	8	6	9
	New 1	10	6	4	9
	New 2	10	1	0	2
Contaminants	V1	10	0	0	3
	V2	10	4	2	6
	V3	10	1	0	3
	V4	10	3	0	3
	New 1	10	0	0	0
	New 2	10	0	0	0
Convexities	V1	10	6	4	8
	V2	10	4	3	5
	V3	10	7	6	8
	V4	10	7	4	9
	New 1	10	7	5	8
	New 2	10	2	0	2
Smooth	V1	10	0	0	0
	V2	10	0	0	0
	V3	10	0	0	0
	V4	10	0	0	0
	New 1	10	0	0	0
	New 2	10	0	0	1

TABLE 5.9

Comparison of the number of defects per unit area on the surface of new and used PVC/NBR gloves (Dunn's method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		**Origin**					
		V1	V2	V3	V4	New 1	New 2
Cavities	V1						
	V2	NS					
	V3	NS	<0.05				
	V4	NS	NS	NS			
	New 1	NS	NS	NS	NS		
	New 2	<0.05	NS	<0.05	<0.05	<0.05	
Contaminants	V1						
	V2	NS					
	V3	NS	NS				
	V4	NS	NS	NS			
	New 1	NS	<0.05	NS	NS		
	New 2	NS	<0.05	NS	NS	NS	
Convexities	V1						
	V2	NS					
	V3	NS	NS				
	V4	NS	NS	NS			
	New 1	NS	NS	NS	NS		
	New 2	<0.05	NS	<0.05	<0.05	<0.05	
Smooth	V1						
	V2	NS					
	V3	NS	NS				
	V4	NS	NS	NS			
	New 1	NS	NS	NS	NS		
	New 2	<0.05	<0.05	<0.05	<0.05	<0.05	

5.3.1.5 Thin polyvinyl chloride gloves

There were only three thin PVC gloves collected and they came from the same OR source and therefore were subjected to the same conditions. These gloves could not be identified by any of the retailers and therefore there were no new ones for comparison. In these circumstances descriptive statistics were the only appropriate means of summarising their defects as depicted in Table 5.10.

TABLE 5.10

Defects per unit area on the surface of used thin unsupported PVC gloves from the same orchardist. The means and standard errors, medians, 25th and 75th percentiles, K-S distances and P values are shown.

Defects	Σ	Mean ± se	Median	25%	75%	K-S	P value
Cracks	3	0.10 ± 0.05	0	0	0	0.528	NS
Cavities	181	6.03 ± 0.44	6	5	7	0.194	<0.01
Convexities	63	2.10 ± 0.50	1	0	4	0.279	<0.001
Contaminants	149	4.97 ± 0.66	5	2	7	0.127	<0.01

5.3.1.6 Maintenance factors

An analysis of the maintenance factors of the gloves from TF was not done because all had been treated in the same manner, therefore there was no information to be gained from a further statistical analysis from this source. This included all the NBR gloves. The NR gloves were all the same age and, as, the other factors were confounded these were not statistically analysed. The thin PVC and PVC/NBR groups were too small to analyse.

Analysis of the maintenance factors of the PVC gloves was problematical because the storage and washing factors were confounded. This only left the age of the gloves to compare with the defects, which are detailed in Tables 5.11 and 5.12. The two year old gloves formed the predominant age group. The difference between the age of the gloves and the number of cracks was not significant ($H = 9.69$, d.f. = 5, $P = 0.0846$). There were differences between cavities and age of the gloves ($H = 31.1$, d.f. = 5, $P < 0.0001$). Contaminants and convexities differed strongly between their age groups ($H = 39.2$, d.f. = 5, $P < 0.0001$; $H = 47.2$, d.f. = 5, $P < 0.0001$) respectively. There was only one smooth area and this was located in the OR group.

TABLE 5.11

Defects per unit area on the surface of used PVC gloves from within different age groups. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Age	n	Median	25%	75%
Cavities	2 months	20	5	4	8
	1 year	40	4	4	7
	2 years	130	3	1	6
	3 Years	20	5	3	6
	4 years	20	10	8	11
	5 years	40	4	2	7
Contaminants	2 months	20	5	2	6
	1 year	40	4	2	6
	2 years	130	7	4	9
	3 Years	20	9	8	10
	4 years	20	7	5	12
	5 years	40	5	2	8
Convexities	2 months	20	4	2	6
	1 year	40	0	0	0
	2 years	130	0	0	0
	3 Years	20	0	0	3
	4 years	20	3	0	5
	5 years	40	0	0	6

TABLE 5.12

Comparison of the number of defects per unit area on the surface of used PVC gloves between different age groups (Dunn's method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		**Age of gloves**					
Cavities		2 months	1 year	2 years	3 years	4 years	5 years
	2 months						
	1 year	NS					
	2 years	NS	NS				
	3 years	NS	NS	NS			
	4 years	NS	<0.05	<0.05	<0.05		
	5 years	NS	NS	NS	NS	<0.05	
Contaminants	2 months						
	1 year	NS					
	2 years	NS	<0.05				
	3 years	<0.05	<0.05	NS			
	4 years	NS	<0.05	NS	NS		
	5 years	NS	NS	NS	<0.05	<0.05	
Convexities	2 months						
	1 year	<0.05					
	2 years	<0.05	NS				
	3 years	<0.05	NS	NS			
	4 years	NS	<0.05	<0.05	NS		
	5 years	<0.05	NS	NS	NS	NS	

5.3.2 Polyvinyl chloride gloves: immersion experiments

Three experiments are integrated in this section: 1) immersion of the external surfaces; 2) one minute immersions; and 3) the immersion of both surfaces.

5.3.2.1 Immersion of the external surfaces of polyvinyl chloride glove fingers in Jetdip®

These experiments are divided into their three time spans as twenty-four hours, thirty-six hours and forty-eight hours.

5.3.2.1.1 *Polyvinyl chloride fingers immersed in Jetdip® for twenty-four hours*

There was no evidence of crazing or slumping on the surfaces of PVC fingers in these experiments. Cracks were only present in the new gloves and therefore there were differences between the treatments ($H = 10.7$, d.f. = 2, $P = 0.0047$). Cavities differed between treatments ($H = 8.12$, d.f. = 2, $P = 0.0173$). Convexities did not differ between treatments ($H = 4.07$, d.f. = 2, $P = 0.131$). There were no differences for smooth areas between the treatments ($H = 0$, d.f. = 2, $P = 1.0000$). Contaminants

differed strongly between treatments (H = 21.1, d.f. = 2, P <0.0001). A summary of the defects is presented in Tables 5.13 and 5.14.

TABLE 5.13

Defects per unit area on the surface of new PVC glove fingers that had been immersed in concentrated or diluted Jetdip® for 24 hours. The medians and percentiles (25th and 75th) are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatments	n	Median	25%	75%
Cavities	New	20	0	0	0
	Diluted	20	1	0	1
	Concentrated	20	1	0	1
Convexities	New	20	0	0	0
	Diluted	20	1	0	1
	Concentrated	20	1	0	1
Contaminants	New	20	3	1	4
	Diluted	20	0	0	1
	Concentrated	20	0	0	1
Cracks	New	20	0	0	1
	Diluted	20	0	0	0
	Concentrated	20	0	0	0
Smooth	New	20	0	0	1
	Diluted	20	0	0	1
	Concentrated	20	0	0	1

TABLE 5.14

Comparison of the number of defects per unit area on the external surface of new PVC glove fingers that had been immersed in concentrated or diluted Jetdip® for 24 hours. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects	Treatments			
		New	Diluted	Concentrated
Cavities	New			
	Diluted	NS		
	Concentrated	NS	NS	
Contaminants	New			
	Diluted	<0.05		
	Concentrated	<0.05	NS	
Cracks	New			
	Diluted	NS		
	Concentrated	NS	NS	

5.3.2.1.2 *Polyvinyl chloride fingers immersed in Jetdip® for thirty-six hours*
There were no cracks in the treated samples (H = 10.7, d.f. = 2, P = 0.0047). Cavities differed strongly between treatments (H = 33.5, d.f. = 2, P <0.0001). Convexities differed convincingly between treatments (H = 18.3, d.f. = 2, P <0.0001). Smooth areas varied between treatments (H = 15.6, d.f. = 2, P = 0.0004). Contaminants differed between treatments (H = 10.1, d.f. = 2, P = 0.0064). These results are illustrated in Tables 5.15 and 5.16.

TABLE 5.15

Defects per unit area on the surface of new PVC glove fingers that had been immersed in concentrated or diluted Jetdip® for 36 hours. The medians and percentiles (25th and 75th) are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatments	n	Median	25%	75%
Cavities	New	20	0	0	0
	Diluted	20	4	2	5
	Concentrated	20	3	3	4
Convexities	New	20	0	0	0
	Diluted	20	3	2	4
	Concentrated	20	3	1	5
Contaminants	New	20	3	1	4
	Diluted	20	0	0	2
	Concentrated	20	1	0	2
Cracks	New	20	0	0	1
	Diluted	20	0	0	0
	Concentrated	20	0	0	0
Smooth	New	20	0	0	1
	Diluted	20	0	0	0
	Concentrated	20	0	0	0

TABLE 5.16

Comparison of the number of defects per unit area on the external surface of new PVC glove fingers that had been immersed in concentrated or diluted Jetdip® for 36 hours (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects	Treatments			
		New	Diluted	Concentrated
Cavities	New			
	Diluted	<0.05		
	Concentrated	<0.05	NS	
Contaminants	New			
	Diluted	<0.05		
	Concentrated	<0.05	NS	
Convexities	New			
	Diluted	<0.05		
	Concentrated	<0.05	NS	
Cracks	New			
	Diluted	NS		
	Concentrated	NS	NS	
Smooth	New			
	Diluted	NS		
	Concentrated	NS	NS	

5.3.2.1.3 *Polyvinyl chloride fingers immersed in Jetdip® for forty-eight hours*
Cracks varied between treatments (H = 10.7, d.f. = 2, P = 0.0047). Cavities differed strongly between treatments (H = 25.3, d.f. = 2, P <0.0001). Convexities varied between treatments (H = 12.9, d.f. = 2, P = 0.0016). There were differences between the treatments for the smooth areas (H = 10, d.f. = 2, P = 0.0067). Contaminants differed strongly between treatments (H = 16.9, d.f. = 2, P = 0.0002). The data are summarised in Tables 5.17 and 5.18.

TABLE 5.17

Defects per unit area on the surface of new PVC glove fingers that had been immersed in concentrated or diluted Jetdip® for 48 hours. The medians and percentiles (25th and 75th) are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatments	n	Median	25%	75%
Cavities	New	20	0	0	0
	Diluted	20	1	0	3
	Concentrated	20	3	1	5
Convexities	New	20	0	0	0
	Diluted	20	3	2	4
	Concentrated	20	1	0	4
Contaminants	New	20	3	1	4
	Diluted	20	0	0	1
	Concentrated	20	2	0	1
Cracks	New	20	0	0	1
	Diluted	20	0	0	0
	Concentrated	20	0	0	0
Smooth	New	20	0	0	1
	Diluted	20	0	0	0
	Concentrated	20	0	0	0

TABLE 5.18

Comparison of the number of defects per unit area on the external surface of new PVC glove fingers that had been immersed in concentrated or diluted Jetdip® for 48 hours (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		Treatments		
		New	Diluted	Concentrated
Cavities	New			
	Diluted	<0.05		
	Concentrated	<0.05	<0.05	
Contaminants	New			
	Diluted	<0.05		
	Concentrated	<0.05	<0.05	
Convexities	New			
	Diluted	<0.05		
	Concentrated	<0.05	<0.05	
Cracks	New			
	Diluted	NS		
	Concentrated	NS	NS	
Smooth	New			
	Diluted	NS		
	Concentrated	NS	NS	

5.3.2.2 Immersion of the external surfaces of polyvinyl chloride fingers in Lorsban®

This group of experiments is sub-sectioned into three time spans.

5.3.2.2.1 *Polyvinyl chloride fingers immersed in Lorsban® for twenty-four hours*

There were differences between treatments for cracks ($H = 10.7$, d.f. = 2, $P = 0.0047$). There were major differences between treatments for cavities ($H = 25.9$, d.f. = 2, $P < 0.0001$). Convexities differed between treatments ($H = 13.2$, d.f. = 2, $P = 0.0013$). Smooth areas differed between treatments ($H = 7.82$, d.f. = 2, $P = 0.0200$). There were strong differences between treatments for contaminants ($H = 18.4$, d.f. = 2, $P < 0.0001$). The data are summarised in Tables 5.19 and 5.20.

TABLE 5.19

Defects per unit area on the surface of new PVC glove fingers that had been immersed in concentrated or diluted Lorsban® for 24 hours. The medians and percentiles (25th and 75th) are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatments	n	Median	25%	75%
Cavities	New	20	0	0	0
	Diluted	20	4	2	5
	Concentrated	20	4	2	5
Convexities	New	20	0	0	0
	Diluted	20	2	2	4
	Concentrated	20	2	2	6
Contaminants	New	20	3	1	4
	Diluted	20	0	0	1
	Concentrated	20	0	0	2
Cracks	New	20	0	0	1
	Diluted	20	0	0	0
	Concentrated	20	0	0	0
Smooth	New	20	0	0	1
	Diluted	20	0	0	0
	Concentrated	20	0	0	1

TABLE 5.20

Comparison of the number of defects per unit area on the external surface of new PVC glove fingers that had been immersed in concentrated or diluted Lorsban® for 24 hours (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects	**Treatments**			
		New	Diluted	Concentrated
Cavities	New			
	Diluted	<0.05		
	Concentrated	<0.05	NS	
Contaminants	New			
	Diluted	<0.05		
	Concentrated	<0.05	NS	
Convexities	New			
	Diluted	<0.05		
	Concentrated	<0.05	NS	
Cracks	New			
	Diluted	NS		
	Concentrated	NS	NS	
Smooth	New			
	Diluted	NS		
	Concentrated	NS	NS	

5.3.2.2.2 *Polyvinyl chloride fingers immersed in Lorsban® for thirty-six hours*
There were differences between treatments for cracks (H = 15.8, d.f. = 3, P = 0.0013). Cavities differed strongly between treatments (H = 41.6, d.f. = 3, P <0.0001). Convexities differed markedly between treatments (H = 30.8, d.f. = 3, P <0.0001). Smooth areas varied between treatments (H = 18.7, d.f. = 3, P = 0.0003). There were strong differences for contaminants between treatments (H = 25.3, d.f. = 3, P <0.0001). The data are summarised in Tables 5.21 and 5.22.

TABLE 5.21

Defects per unit area on the surface of new PVC glove fingers that had been immersed in concentrated or diluted Lorsban® for 36 hours. The medians and percentiles (25th and 75th) are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatments	n	Median	25%	75%
Cavities	New	20	0	0	0
	Diluted	20	3	2	4
	Concentrated	20	2	1	3
	Taped finger	20	2	1	2
Convexities	New	20	0	0	0
	Diluted	20	3	3	4
	Concentrated	20	2	1	2
	Taped finger	20	2	1	2
Contaminants	New	20	3	1	4
	Diluted	20	1	0	3
	Concentrated	20	2	0	3
	Taped finger	20	0	0	0
Cracks	New	20	0	0	1
	Diluted	20	0	0	0
	Concentrated	20	0	0	0
	Taped finger	20	0	0	0
Smooth	New	20	0	0	1
	Diluted	20	0	0	0
	Concentrated	20	0	0	0
	Taped finger	20	0	0	0

TABLE 5.22

Comparison of the number of defects per unit area on the external surface of new PVC glove fingers that had been immersed in concentrated or diluted Lorsban® for 36 hours (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		**Treatments**			
		New	Diluted	Concentrated	Taped finger
Cavities	New				
	Diluted	<0.05			
	Concentrated	<0.05	<0.05		
	Taped finger	<0.05	<0.05	NS	
Contaminants	New				
	Diluted	<0.05			
	Concentrated	<0.05	NS		
	Taped finger	<0.05	<0.05	<0.05	
Convexities	New				
	Diluted	<0.05			
	Concentrated	<0.05	<0.05		
	Taped finger	<0.05	<0.05	NS	
Cracks	New				
	Diluted	NS			
	Concentrated	NS	NS		
	Taped finger	NS	NS	NS	
Smooth	New				
	Diluted	NS			
	Concentrated	NS	NS		
	Taped finger	NS	NS	NS	

5.3.2.2.3 *Polyvinyl chloride fingers immersed in Lorsban® for forty-eight hours*

Cracks differed between treatments (H = 15.8, d.f. = 3, P = 0.0013). There were differences for cavities between treatments (H = 9.77, d.f. = 3, P = 0.0206). Convexities did not vary between the treatments (H = 4.77, d.f. = 3, P = 0.190). Smooth areas did not differ between treatments (H = 6.53, d.f. = 3, P = 0.0886). There were strong differences between treatments for contaminants (H = 21.3, d.f. = 3, P <0.0001). The data are summarised in Tables 5.23 and 5.24.

TABLE 5.23

Defects per unit area on the surface of new PVC glove fingers that had been immersed in concentrated or diluted Lorsban® for 48 hours. The medians and percentiles (25th and 75th) are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatments	n	Median	25%	75%
Cavities	New	20	0	0	0
	Diluted	20	2	0	2
	Concentrated	20	1	0	0
	Taped finger	20	2	0	3
Convexities	New	20	0	0	0
	Diluted	20	1	0	1
	Concentrated	20	1	0	1
	Taped finger	20	2	0	2
Contaminants	New	20	3	1	4
	Diluted	20	0	0	2
	Concentrated	20	0	0	1
	Taped finger	20	0	0	1
Cracks	New	20	0	0	1
	Diluted	20	0	0	0
	Concentrated	20	0	0	0
	Taped finger	20	0	0	0
Smooth	New	20	0	0	1
	Diluted	20	0	0	0
	Concentrated	20	0	0	1
	Taped finger	20	0	0	1

TABLE 5.24

Comparison of the number of defects per unit area on the external surface of new PVC glove fingers that had been immersed in concentrated or diluted Lorsban® for 48 hours (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		**Treatments**			
		New	Diluted	Concentrated	Taped finger
Cavities	New				
	Diluted	<0.05			
	Concentrated	<0.05	NS		
	Taped finger	<0.05	NS	NS	
Contaminants	New				
	Diluted	<0.05			
	Concentrated	<0.05	NS		
	Taped finger	<0.05	NS	NS	
Cracks	New				
	Diluted	NS			
	Concentrated	NS	NS		
	Taped finger	NS	NS	NS	

5.3.2.3 One minute immersion of polyvinyl chloride glove fingers

There were two experiments in this sub-section; immersion in Jetdip® and in Lorsban®.

5.3.2.3.1 *Polyvinyl chloride fingers immersed in Jetdip®*

There were no differences between treatments for cracks (T = 360, P = 0.1770). Cavities differed between treatments (T = 576, P <0.0001). Convexities differed strongly between treatments (T = 544.5, P <0.0001). There were no differences between treatments for smooth areas (T = 480, P = 0.0583). Contaminants varied convincingly between treatments (T = 580, P <0.0001). A summary of the data is presented in Table 5.25.

TABLE 5.25

Defects per unit area on the surface of new PVC glove fingers that had been immersed in Jetdip® for one minute. The medians and percentiles (25th and 75th) are shown (Mann-Whitney Rank Sum Test).

Defects	Glove finger	n	Median	25%	75%
Cavities	New	20	0	0	0
	Immersed	20	2	2	4
Convexities	New	20	0	0	0
	Immersed	20	2	2	5
Contaminants	New	20	3	1	4
	Immersed	20	0	0	0
Cracks	New	20	0	0	0
	Immersed	20	0	0	1
Smooth	New	20	0	0	1
	Immersed	20	0	0	0

5.3.2.3.2 *Polyvinyl chloride fingers immersed in Lorsban®*

There were no differences between the untreated and treated fingers for cracks ($T = 8$, $P = 0.7260$). Cavities differed strongly between the untreated and treated fingers ($T = 259.5$, $P < 0.0001$). Convexities also differed, but not as strongly ($T = 528.5$, $P = 0.00139$). Smooth areas did not vary between treatments ($T = 340$, $P = 0.0583$). Contaminants differed between treatments ($T = 318.5$, $P = 0.0138$). A summary of the data is presented in Table 5.26.

TABLE 5.26

Defects per unit area on the surface of new PVC glove fingers that had been immersed in Lorsban® for one minute. The medians and percentiles (25th and 75th) are shown (Mann-Whitney Rank Sum Test).

Defects	Glove Finger	n	Median	25%	75%
Cavities	New	20	0	0	0
	Immersed	20	3	1	3
Convexities	New	20	0	0	0
	Immersed	20	3	2	4
Contaminants	New	20	3	1	4
	Immersed	20	0	0	2
Cracks	New	20	0	0	0
	Immersed	20	0	0	1
Smooth	New	20	0	0	1
	Immersed	20	0	0	0

5.3.2.4 Immersion of both surfaces of polyvinyl chloride gloves

These experiments are divided into three different time spans; twenty-four hours, thirty-six hours and forty-eight hours.

5.3.2.4.1 *Polyvinyl chloride gloves immersed in Top Clip Blue Shield® for twenty-four hours*

There were no smooth areas on these samples. There were some cracks, but these were not significant ($H = 5.70$, d.f. = 2, $P = 0.0579$). Cavities differed between treatments ($H = 6.47$, d.f. = 2, $P = 0.0394$). There were marked differences between the treatments for convexities ($H = 23.2$, d.f. = 2, $P < 0.0001$) and for contaminants ($H = 12.4$, d.f. = 2, $P = 0.0021$). A summary of the findings is presented in Tables 5.27 and 5.28.

TABLE 5.27

Defects per unit area on the surface of new PVC gloves that had been immersed in Top Clip Blue Shield® for 24 hours. The treatments were: washed in distilled water immediately post treatment; unwashed; and new, which were untreated. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatments	n	Median	25%	75%
Cavities	New	20	2	2	3
	Washed	20	1	1	2
	Unwashed	20	2	1	3
Contaminants	New	20	1	0	2
	Washed	20	3	1	3
	Unwashed	20	2	1	3
Convexities	New	20	2	1	4
	Washed	20	1	0	1
	Unwashed	20	0	0	1
Cracks*	New	20	0	0	0
	Washed	20	0	0	0
	Unwashed	20	0	0	0

* The mean for cracks = 0.15

TABLE 5.28

Comparison of defects per unit area on the surface of new PVC gloves that had been immersed in Top Clip Blue Shield® for 24 hours (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		Treatments		
		New	Washed	Unwashed
Cavities	New			
	Washed	<0.05		
	Unwashed	NS	NS	
Contaminants	New			
	Washed	<0.05		
	Unwashed	<0.05	NS	
Convexities	New			
	Washed	<0.05		
	Unwashed	<0.05	<0.05	

5.3.2.4.2 *Polyvinyl chloride gloves immersed in Top Clip Blue Shield® for thirty-six hours*

Defects found on the PVC gloves that had been immersed in Top Clip Blue Shield® for thirty-six hours are highlighted in Tables 5.29 and 5.30. There were no cracks in these samples. The number of cavities differed by treatment ($H = 21.9$, d.f. = 2, $P < 0.0001$). Convexities varied strongly between treatments ($H = 21.1$, d.f. = 2, $P < 0.0001$). Smooth areas also differed by treatments ($H = 18.2$, d.f. = 2, $P < 0.0001$). Contaminants varied between treatments ($H = 14.3$, d.f. = 2, $P < 0.0001$).

TABLE 5.29

Defects per unit area on the surface of new PVC gloves that had been immersed in Top Clip Blue Shield® for 36 hours. The treatments were: washed in distilled water immediately post treatment; unwashed; and new, which were untreated. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatment	n	Median	25%	75%
Cavities	New	20	2	2	3
	Washed	20	2	1	3
	Unwashed	20	2	2	3
Contaminants	New	20	1	0	2
	Washed	20	0	0	0
	Unwashed	20	0	0	0
Convexities	New	20	2	1	4
	Washed	20	1	0	2
	Unwashed	20	2	2	3
Smooth	New	20	0	0	0
	Washed	20	0	0	1
	Unwashed	20	0	0	0

TABLE 5.30

Comparison of defects per unit area on the surface of new PVC gloves that had been immersed in Top Clip Blue Shield® for 36 hours. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects	Treatments			
		New	Washed	Unwashed
Cavities	New			
	Washed	<0.05		
	Unwashed	NS	<0.05	
Contaminants	New			
	Washed	<0.05		
	Unwashed	<0.05	NS	
Convexities	New			
	Washed	<0.05		
	Unwashed	NS	<0.05	
Smooth	New			
	Washed	NS		
	Unwashed	NS	NS	

5.3.2.4.3 *Polyvinyl chloride gloves immersed in Top Clip Blue Shield® for forty-eight hours*

The defects detected on the surface of PVC glove samples following immersion in Top Clip Blue Shield® for forty-eight hours are presented in Tables 5.31 and 5.32. There were no smooth areas on these samples. Cracks differed between the treatments and there were none in the new samples ($H = 38.3$, d.f. = 2, $P < 0.0001$). There were more cavities in the unwashed samples and they varied between treatments ($H = 21.8$, d.f. = 2, $P < 0.0001$). Convexities were also more plentiful on the unwashed samples and differed between treatments ($H = 14.3$, d.f. = 2, $P = 0.0008$). Contaminants varied between treatments ($H = 27.4$, d.f. = 2, $P < 0.0001$).

TABLE 5.31

Defects per unit area on the surface of new PVC gloves that had been immersed in Top Clip Blue Shield® for 48 hours. The treatments were: washed in distilled water immediately post treatment; unwashed; and new, which were untreated. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatments	n	Median	25%	75%
Cavities	New	20	2	2	3
	Washed	20	2	1	2
	Unwashed	20	5	3	8
Contaminants	New	20	1	0	2
	Washed	20	0	0	0
	Unwashed	20	1	0	2
Convexities	New	20	2	1	4
	Washed	20	1	0	2
	Unwashed	20	2	1	4
Cracks	New	20	0	0	0
	Washed	20	2	2	4
	Unwashed	20	0	0	0

TABLE 5.32

Comparison of defects per unit area on the surface of new PVC gloves that had been immersed in Top Clip Blue Shield® for 48 hours. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		Treatments		
		New	Washed	Unwashed
Cavities	New			
	Washed	<0.05		
	Unwashed	<0.05	<0.05	
Contaminants	New			
	Washed	<0.05		
	Unwashed	<0.05	<0.05	
Convexities	New			
	Washed	<0.05		
	Unwashed	NS	<0.05	
Cracks	New			
	Washed	<0.05		
	Unwashed	<0.05	<0.05	

5.3.3 Nitrile-butadiene rubber gloves: immersion experiments

This section covers three groups of experiments with Sol-Vex™ gloves: immersion of the external surfaces; one minute immersion experiments; and immersion of both surfaces.

5.3.3.1 Immersion of the external surfaces of nitrile-butadiene rubber gloves in Jetdip®

Crazes, slumps and smooth areas were not observed on these samples in these experiments. These groups of experiments are presented in their three time spans.

5.3.3.1.1 *Nitrile-butadiene rubber gloves immersed in Jetdip® for twenty-four hours*

There were strong differences for cracks between treatments ($H = 43.1$, d.f. = 2, $P < 0.0001$). Cavities did not differ between treatments ($H = 0.0986$, d.f. = 2, $P = 0.952$). Convexities varied markedly between treatments ($H = 35.2$, d.f. = 2, $P < 0.0001$). Contaminants varied between treatments ($H = 12.2$, d.f. = 2, $P = 0.0023$). The data are presented in Tables 5.33 and 5.34.

TABLE 5.33

Defects per unit area on the surface of new NBR gloves that had been immersed in concentrated or diluted Jetdip® for 24 hours. The medians and percentiles are shown (25th and 75th). (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatments	n	Median	25%	75%
Cavities	New	20	4	4	5
	Diluted	20	5	3	6
	Concentrated	20	5	3	5
Contaminants	New	20	0	0	0
	Diluted	20	0	0	2
	Concentrated	20	0	0	0
Convexities	New	20	3	3	4
	Diluted	20	0	0	4
	Concentrated	20	8	6	9
Cracks	New	20	0	0	0
	Diluted	20	6	5	8
	Concentrated	20	4	3	5

TABLE 5.34

Comparison of defects per unit area on the surface of NBR glove samples that had been immersed in concentrated or diluted Jetdip® for 24 hours. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		**Treatments**		
		New	Diluted	Concentrated
Contaminants	New			
	Diluted	<0.05		
	Concentrated	NS	<0.05	
Convexities	New			
	Diluted	<0.05		
	Concentrated	<0.05	<0.05	
Cracks	New			
	Diluted	<0.05		
	Concentrated	<0.05	<0.05	

5.3.3.1.2 *Nitrile-butadiene rubber gloves immersed in Jetdip® for thirty-six hours*
Cracks varied convincingly between treatments (H = 45.8, d.f. = 2, P <0.0001). There were no differences for cavities between treatments (H = 5.80, d.f. = 2, P = 0.0550). Convexities varied between treatments (H = 19.6, d.f. = 2, P <0.0001). There were variations between treatments for contaminants (H = 9.97, d.f. = 2, P = 0.0068). A summary of the data is presented in Tables 5.35 and 5.36.

TABLE 5.35

Defects per unit area on the surface of new NBR gloves that had been immersed in concentrated or diluted Jetdip® for 36 hours. The medians and percentiles (25th and 75th) are shown. (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatments	n	Median	25%	75%
Cavities	New	20	4	4	5
	Diluted	20	4	3	4
	Concentrated	20	3	2	5
Contaminants	New	20	0	0	0
	Diluted	20	0	0	0
	Concentrated	20	0	0	2
Convexities	New	20	3	3	4
	Diluted	20	1	0	3
	Concentrated	20	5	3	7
Cracks	New	20	0	0	0
	Diluted	20	4	3	4
	Concentrated	20	6	4	7

TABLE 5.36

Comparison of defects per unit area on the surface of NBR glove samples that had been immersed in concentrated or diluted Jetdip® for 36 hours. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		Treatments		
		New	Diluted	Concentrated
Contaminants	New			
	Diluted	NS		
	Concentrated	NS	NS	
Convexities	New			
	Diluted	<0.05		
	Concentrated	<0.05	<0.05	
Cracks	New			
	Diluted	<0.05		
	Concentrated	<0.05	<0.05	

5.3.3.1.3 *Nitrile-butadiene rubber gloves immersed in Jetdip® for forty-eight hours*

Cracks differed strongly between treatments (H = 40.9, d.f. = 2, P <0.0001). There were strong differences for cavities (H = 20.2, d.f. = 2, P <0.0001). Convexities varied between treatments (H = 10.3, d.f. = 2, P = 0.0057). There were variations for contaminants between treatments (H = 10.3, d.f. = 2, P = 0.0058). The data are presented in Tables 5.37 and 5.38.

TABLE 5.37

Defects per unit area on the surface of new NBR gloves that had been immersed in concentrated or diluted Jetdip® for 48 hours. The medians and percentiles (25th and 75th) are shown. (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatments	n	Median	25%	75%
Cavities	New	20	4	4	5
	Diluted	20	6	6	9
	Concentrated	20	5	4	7
Contaminants	New	20	0	0	0
	Diluted	20	0	0	0
	Concentrated	20	0	0	3
Convexities	New	20	3	3	4
	Diluted	20	6	4	8
	Concentrated	20	5	4	7
Cracks	New	20	0	0	0
	Diluted	20	5	4	7
	Concentrated	20	4	3	5

TABLE 5.38

Comparison of defects per unit area on the surface of NBR glove samples that had been immersed in concentrated or diluted Jetdip® for 48 hours. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects	Treatments			
		New	Diluted	Concentrated
Cavities	New			
	Diluted	<0.05		
	Concentrated	<0.05	<0.05	
Contaminants	New			
	Diluted	NS		
	Concentrated	NS	NS	
Convexities	New			
	Diluted	<0.05		
	Concentrated	<0.05	NS	
Cracks	New			
	Diluted	<0.05		
	Concentrated	<0.05	NS	

5.3.3.2 Immersion of the external surfaces of nitrile-butadiene rubber gloves in Lorsban®

This section is subdivided into three time spans. There were no crazes, slumps or smooth areas observed on the samples in these experiments.

5.3.3.2.1 *Nitrile-butadiene rubber gloves immersed in Lorsban® for twenty-four hours*

There were marked differences for cracks between treatments (H = 42.6, d.f. = 2, P <0.0001). Cavities did not differ between treatments (H = 2.36, d.f. = 2, P = 0.307). There was some variation between treatments for convexities (H = 9.76, d.f. = 2, P = 0.0076). Contaminants varied between treatments (H = 6.21, d.f. = 2, P = 0.0448). The data are summarised in Tables 5.39 and 5.40.

TABLE 5.39

Defects per unit area on the surface of new NBR gloves that had been immersed in concentrated or diluted Lorsban® for 24 hours. The medians and percentiles (25th and 75th) are shown. (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatments	n	Median	25%	75%
Cavities	New	20	4	4	5
	Diluted	20	4	3	7
	Concentrated	20	4	2	5
Contaminants*	New	20	0	0	0
	Diluted	20	0	0	0
	Concentrated	20	0	0	0
Convexities	New	20	3	3	4
	Diluted	20	6	4	7
	Concentrated	20	2	0	6
Cracks	New	20	0	0	0
	Diluted	20	7	5	8
	Concentrated	20	6	5	7

* The mean for contaminants = 0.1

TABLE 5.40

Comparison of defects per unit area on the surface of NBR glove samples that had been immersed in concentrated or diluted Lorsban® for 24 hours. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		Treatments		
		New	Diluted	Concentrated
Contaminants	New			
	Diluted	NS		
	Concentrated	NS	NS	
Convexities	New			
	Diluted	<0.05		
	Concentrated	NS	<0.05	
Cracks	New			
	Diluted	<0.05		
	Concentrated	<0.05	NS	

5.3.3.2.2 *Nitrile-butadiene rubber gloves immersed in Lorsban® for thirty-six hours*

There were marked variations for cracks between treatments (H = 42.6, d.f. = 2, P <0.0001). Cavities did not differ between treatments (H = 1.99, d.f. = 2, P = 0.370). Convexities differed between treatments (H = 9.76, d.f. = 2, P = 0.0076). Contaminants varied between treatments (H = 6.21, d.f. = 2, P = 0.04448). The data are summarised in Tables 5.41 and 5.42.

TABLE 5.41

Defects per unit area on the surface of new NBR gloves that had been immersed in concentrated or diluted Lorsban® for 36 hours. The medians and percentiles (25th and 75th) are shown. (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatments	n	Median	25%	75%
Cavities	New	20	4	4	5
	Diluted	20	4	2	7
	Concentrated	20	4	2	5
Contaminants*	New	20	0	0	0
	Diluted	20	0	0	0
	Concentrated	20	0	0	0
Convexities	New	20	3	3	4
	Diluted	20	6	4	7
	Concentrated	20	2	0	6
Cracks	New	20	0	0	0
	Diluted	20	7	5	8
	Concentrated	20	6	5	7

* The mean for contaminants = 0.32

TABLE 5.42

Comparison of defects per unit area on the surface of NBR glove samples that had been immersed in concentrated or diluted Lorsban® for 36 hours. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		Treatments		
		New	Diluted	Concentrated
Contaminants	New			
	Diluted	NS		
	Concentrated	NS	NS	
Convexities	New			
	Diluted	<0.05		
	Concentrated	NS	<0.05	
Cracks	New			
	Diluted	<0.05		
	Concentrated	<0.05	NS	

5.3.3.2.3 *Nitrile-butadiene rubber gloves immersed in Lorsban® for forty-eight hours*

There were strong differences for cracks between treatments (H = 41.3, d.f. = 2, P <0.0001). Contaminants varied between treatments (H = 10.7, d.f. = 2, P = 0.0047). Cavities did not differ between treatments ($F_{2,57}$ = 2.24, P = 0.115) nor did convexities ($F_{2,57}$ = 1.37, P = 0.262). However, the power of this test was low and therefore this result invites caution. The results are presented in Tables 5.43 and 5.44.

TABLE 5.43

Defects per unit area on the surface of new NBR gloves that had been immersed in concentrated or diluted Lorsban® for 48 hours. The medians and percentiles (25th and 75th) are shown (Kruskal-Wallis One Way ANOVA on Ranks). Convexities and cavities were normally distributed and their means and standard errors are shown in the lower section of the table.

Defects	Treatments	n	Median	25%	75%
Contaminants	New	20	0	0	0
	Diluted	20	0	0	0
	Concentrated	20	0	0	1
Cracks	New	20	0	0	0
	Diluted	20	6	4	6
	Concentrated	20	5	4	7
			Mean ± se		
Cavities	New	20	4 ± 0		
	Diluted	20	3 ± 0		
	Concentrated	20	5 ± 0		
Convexities	New	20	4 ± 0		
	Diluted	20	4 ± 0		
	Concentrated	20	4 ± 1		

TABLE 5.44

Comparison of defects per unit area on the surface of NBR gloves that had been immersed in concentrated or diluted Lorsban® for 48 hours. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		Treatments		
		New	Diluted	Concentrated
Contaminants	New			
	Diluted	NS		
	Concentrated	NS	NS	
Cracks	New			
	Diluted	<0.05		
	Concentrated	<0.05	NS	

5.3.3.3 One minute immersion of nitrile-butadiene rubber gloves

There were no smooth areas, slumps or crazes observed in these experiments.

5.3.3.3.1 *Nitrile-butadiene rubber gloves immersed in Jetdip®*

There were no differences between treatments for cracks (T = 390, P = 0.5940). Cavities did not differ between treatments (T = 455, P = 0.228). Convexities did not vary between treatments (T = 445, P = 0.3504). There were no differences for contaminants between treatments (T = 380, P = 420). The data are summarised in Table 5.45.

TABLE 5.45

Defects per unit area on the surface of new NBR glove fingers that had been immersed in Jetdip® for one minute. The medians and percentiles (25th and 75th) are shown (Mann-Whitney Rank Sum Test).

Defects	Glove finger	n	Median	25%	75%
Cavities	New	20	4	4	5
	Immersed	20	4	3	4
Convexities	New	20	4	3	4
	Immersed	20	4	3	5
Contaminants*	New	20	0	0	0
	Immersed	20	0	0	0
Cracks†	New	20	0	0	0
	Immersed	20	0	0	0

* The mean for contaminants = 0.15
† The mean for cracks = 0.05

5.3.3.3.2 *Nitrile-butadiene rubber gloves immersed in Lorsban®*

Cracks did not differ between the new and the immersed gloves (T = 470, P = 0.105). Cavities differed strongly between treatments (T = 537.5, P <0.0001). Convexities differed between treatments (T = 269, P <0.0001). There were no variations between new and the immersed gloves for contaminants (T = 360, P = 0.177). The data are presented in Table 5.46.

TABLE 5.46

Defects per unit area on the surface of new NBR glove fingers that had been immersed in Lorsban® for one minute. The medians and percentiles (25th and 75th) are shown (Mann-Whitney Rank Sum Test).

Defects	Glove finger	n	Median	25%	75%
Cavities	New	20	4	4	5
	Immersed	20	6	5	8
Convexities	New	20	3	3	4
	Immersed	20	6	5	7
Contaminants	New	20	0	0	0
	Immersed	20	0	0	1
Cracks	New	20	0	0	0
	Immersed	20	0	0	1

5.3.3.4 Immersion of both surfaces of the nitrile-butadiene-rubber gloves

This subsection is divided into three time spans. There were no smooth or crazed areas on the NBR samples in these experiments.

5.3.3.4.1 *New nitrile-butadiene rubber gloves immersed in Top Clip Blue Shield® for twenty-four hours*

Defects in the NBR glove samples are presented in Tables 5.47 and 5.48. Cracks were only observed in the treated samples and there were differences between treatments ($H = 52.4$, d.f. = 2, $P < 0.0001$). Cavities did not differ between treatments ($H = 1.40$, d.f. = 2, $P = 0.497$). Convexities were weakly significant between treatments ($H = 7.70$, d.f. = 2, $P = 0.0212$. Slumps were only noted on the new samples ($H = 13.1$, d.f. = 2, $P = 0.0015$). Contaminants were only found on the samples that had been subjected to the different treatments ($H = 11.9$, d.f. = 2, $P = 0.026$).

TABLE 5.47

Defects per unit area on the surface of new NBR gloves that had been immersed in Top Clip Blue Shield® for 24 hours. The medians and percentiles (25th and 75th) are shown. (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatments	n	Median	25%	75%
Cavities	New	20	1	0	3
	Washed	20	1	0	4
	Unwashed	20	2	1	3
Contaminants	New	20	0	0	0
	Washed	20	0	0	2
	Unwashed	20	0	0	0
Convexities	New	20	2	1	3
	Washed	20	0	0	3
	Unwashed	20	3	2	3
Cracks	New	20	0	0	0
	Washed	20	2	1	3
	Unwashed	20	0	0	0
Slumps	New	20	0	0	2
	Washed	20	0	0	0
	Unwashed	20	0	0	0

TABLE 5.48

Comparison of defects per unit area on the surface of new, washed and unwashed NBR gloves that had been immersed in Top Clip Blue Shield® for 24 hours. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		Treatments		
		New	Washed	Unwashed
Convexities	New			
	Washed	NS		
	Unwashed	<0.05	<0.05	
Contaminants	New			
	Washed	<0.05		
	Unwashed	NS	<0.05	
Cracks	New			
	Washed	<0.05		
	Unwashed	NS	<0.05	
Slumps	New			
	Washed	NS		
	Unwashed	NS	NS	

5.3.3.4.2 *Nitrile-butadiene rubber gloves immersed in Top Clip Blue Shield® for thirty-six hours*

The defects viewed on the surface of NBR gloves are summarised in Tables 5.49 and 5.50. Cracks were present in the treated samples and differed by treatments ($H = 37.6$, d.f. = 2, $P < 0.0001$). Cavities did not vary significantly between treatments ($H = 3.58$, d.f. = 2, $P = 0.167$). The variability of convexities within the treatments was weaker ($H = 12.2$, d.f. = 2, $P = 0.0023$). Slumps were not found on the treated samples ($H = 13.1$, d.f. = 2, $P = 0.0015$). Contaminants were only found on the treated samples and they did differ between groups ($H = 19.2$, d.f. = 2, $P < 0.0001$).

TABLE 5.49

Defects per unit area on the surface of new NBR gloves that had been immersed in Top Clip Blue Shield® for 36 hours. The medians and percentiles (25th and 75th) are shown. (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatments	n	Median	25%	75%
Cavities	New	20	1	0	3
	Washed	20	2	1	2
	Unwashed	20	3	1	4
Contaminants	New	20	0	0	0
	Washed	20	0	0	2
	Unwashed	20	2	0	4
Convexities	New	20	2	1	3
	Washed	20	0	0	0
	Unwashed	20	1	0	4
Cracks	New	20	0	0	0
	Washed	20	3	3	5
	Unwashed	20	0	0	2
Slumps	New	20	0	0	2
	Washed	20	0	0	0
	Unwashed	20	0	0	0

TABLE 5.50

Comparison of defects per unit area on the surface of new, washed and unwashed NBR glove samples that had been immersed in Top Clip Blue Shield® for 36 hours. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects	Treatments			
		New	Washed	Unwashed
Contaminants	New			
	Washed	<0.05		
	Unwashed	<0.05	<0.05	
Convexities	New			
	Washed	<0.05		
	Unwashed	NS	<0.05	
Cracks	New			
	Washed	<0.05		
	Unwashed	<0.05	<0.05	
Slumps	New			
	Washed	NS		
	Unwashed	NS	NS	

5.3.3.4.3 *Nitrile-butadiene rubber gloves immersed in Top Clip Blue Shield® for forty-eight hours*

A summary of the results from NBR glove samples that had been immersed in Top Clip Blue Shield® for forty-eight hours is given in Tables 5.51 and 5.52. Cracks varied between the groups ($H = 40.6$, d.f. = 2, $P < 0.0001$). Cavities did not vary significantly between the groups ($H = 3.29$, d.f. = 2, $P = 0.193$). Convexities differed between groups ($H = 22.8$, d.f. = 2, $P < 0.0001$). There were no slumps on the samples that had been treated ($H = 13.1$, d.f. = 2, $P = 0.0015$). Contaminants did not vary between groups as strongly as the other significant differences ($H = 13.9$, d.f. = 2, $P = 0.001$).

TABLE 5.51

Defects per unit area on the surface of new NBR gloves that had been immersed in Top Clip Blue Shield® for 48 hours. The medians and percentiles (25th and 75th) are shown. (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatments	n	Median	25%	75%
Cavities	New	20	1	0	3
	Washed	20	2	0	3
	Unwashed	20	1	0	3
Contaminants	New	20	0	0	0
	Washed	20	1	0	5
	Unwashed	20	0	0	1
Convexities	New	20	2	1	3
	Washed	20	0	0	1
	Unwashed	20	0	0	0
Cracks	New	20	0	0	0
	Washed	20	1	0	2
	Unwashed	20	4	3	4
Slumps	New	20	0	0	2
	Washed	20	0	0	0
	Unwashed	20	0	0	0

TABLE 5.52

Comparison of defects per unit area on the surface of new, washed and unwashed NBR gloves that had been immersed in Top Clip Blue Shield® for 48 hours. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		Treatments		
Contaminants		New	Washed	Unwashed
	New			
	Washed	<0.05		
	Unwashed	<0.05	NS	
Convexities	New			
	Washed	<0.05		
	Unwashed	<0.05	NS	
Cracks	New			
	Washed	<0.05		
	Unwashed	<0.05	<0.05	
Slumps	New			
	Washed	NS		
	Unwashed	NS	NS	

5.4 Discussion

Usage of CPGs in agricultural enterprises was associated with the development of a range of surface defects. These defects can have a critical impact upon CPG performance and as weathering occurs more defects can be anticipated. The Griffith Theory of Flaws, which states that the discrepancy between the expected strength of the material and the actual strength is due to inherent flaws, can be applied to CPGs. Many defects can give rise to crack propagation that will promote the penetration of solutions. Depressed defects can harbour pesticides and other contaminants, which in turn may penetrate and/or permeate the entire glove material. If the glove is supported, the lining can act as a reservoir and thus increases the potential for dermal exposure. Contaminants can act as abrasive agents and cause physical damage to the gloves. The properties of contaminants may cause chemical damage.

The interpretation of the results of the immersion experiments is incorporated into the PVC and NBR sections.

5.4.1 Polyvinyl chloride gloves

Some cavities were intrinsic to the glove surface because they were a feature of the new gloves and therefore are the result of the manufacturing process. Defects that occur as a result of the manufacturing processes can influence the barrier properties of CPGs. However, when PVC gloves have been in active service, the density of cavities increased (with the exception of the TF group). Most cavities were observed in the four year old group, although there was no significant difference between the two month old gloves and the four year old gloves. The age of the gloves did not linearly correlate with the frequency of cavities. This increased the likelihood that the type of work and environmental exposures were the more important contributing agents.

In the both surfaces immersion experiments cavities were incremental, over the various time sequences, in the unwashed samples. This may be because Top Clip Blue Shield® is quite viscous and volatilisation or dripping off may have been slower than in the washed samples where the remaining Top Clip Blue Shield® would have been very diluted, less viscous and drying time would have been shorter. The unwashed samples were therefore exposed to much higher concentrations of Top Clip Blue Shield® for a longer period, which caused cavities. In the finger immersion experiments there were fewer cavities in the new samples and exposure to both diluted and concentrated Lorsban® and Jetdip® caused cavities. There were slightly less in the samples exposed to Jetdip® for thirty-six hours. This may be because the permeation process was occurring and the material was in the process of swelling.

Cavities were a significant feature of the one minute immersion experiments. It appears that even one minute exposure to Lorsban® and Jetdip® may cause cavities. Although the actual immersion time was one minute the exposure time was greater than this because the drying time must be taken into consideration. The gloves were dried in a vertical position and the sampling was done from the finger tip region. Therefore, the concentrated OPs would have gravitated to this region and because of their viscosity may not have dripped off completely and would have dried on the material.

As was expected contaminants accumulated with glove use. New PVC is tacky and this is conducive to the affixation of particulates such as pollens, fibres, dusts and dirt. This tackiness wears off as the gloves become worn, a combination of contaminants adheres to the gloves and there is no doubt that maintenance factors, *e.g.* washing, would impinge greatly upon the quantity and type of contaminants. Since several of the DP gloves were kept on the floor of a truck, they were exposed to a variety of contaminants. In the finger immersion experiments and the one minute immersion experiments the new gloves had more contaminants on them and again this can be attributed to their tackiness. It was expected that the taped fingers may have had more contaminants on them as they were handled more than the other fingers. However, this was not the case and therefore the immersion and the cleansing processes removed most of the contaminants from the glove fingers. There was no trend evident for the deposition of contaminants in the both surfaces immersion experiment. It can be assumed that some may have settled on the surface and were washed off by the water or the Top Clip Blue Shield®. Others may have adhered to the glove surface during the drying time.

Convexities were a conspicuous feature of the new gloves. All the used groups except DP were different from the new group. Generally, this finding was supported by the aged group analysis where the two month old gloves had more convexities than the older gloves. There were no significant differences between the two month and the four year old gloves, but in both cases, this only constituted one pair of gloves and therefore it would be more beneficial to examine the general trend. A tentative conclusion from these findings is that the convexities may be eroded with use. If this is the case there will be a loss of the surface integrity, which may act as precursor for penetration.

A similar trend is portrayed in the immersion of both surfaces experiments. There was no trend evident within the treated groups, although it is highly probable that permeation occurred following Fickian diffusion. The initial solvation caused swelling or convexities. It is conceivable that the solvents rather than the a.i. were the primary

agents. Exposure to Top Clip Blue Shield® was part of the DP CPGs working history and therefore their similar rates of convexities to the new group may have been due to absorption of the chemical. The other possibility is that DP 1–2 were only two months old and may not have been subject to the same degree of erosion as the older gloves and this issue would have affected the overall DP results.

This trend is not evident with the finger immersion experiments where there were few convexities on the new samples. It is apparent that there were marked differences between the PVC glove batches, a reflection of inadequate quality control procedures in the manufacturing process. Convexities became a significant feature of the treated fingers for all the exposure times for the Lorsban® finger immersion experiments. The fingers exposed to the concentrated Lorsban® for thirty-six and forty-eight hours had a similar number of convexities, which included the taped and un-taped fingers. This eliminates the possibility that permeation occurred from the interior through to the exterior surfaces, *e.g.* from condensation wetting the interior surface, and giving rise to convexities. As both the linings in the taped and un-taped fingers were wet following exposure to concentrated Lorsban® for thirty-six and forty-eight hours, it is likely that permeation occurred and that convexities were a related phenomenon. Exposure to Jetdip® also caused convexities, but these did not become a significant feature until thirty-six and forty-eight hours. Therefore permeation was somewhat slower than with Lorsban®.

In the one minute immersion experiments, convexities were a characteristic of the treated samples suggesting that even at one minute immersion permeation may occur. The actual exposure and drying time need to be considered, as with cavities. However, a minute's exposure, *e.g.* a splash or spill is likely in the farming arena, and it is most unlikely that a glove would be rinsed immediately following a splash or spill even if noticed.

As there were very few cracks found in the new PVC gloves, it can be assumed that cracks are caused by working conditions. Apart from the OR group differing significantly from the TF group there were no differences between the used groups. Only the black PVC gloves had cracks in the BG group, and given that the black PVC looked superior in quality to the red PVC as discussed in Chapter Four (4.3), this was a surprising but not significant observation. One of the working conditions that can be eliminated is the age of the gloves. As expected the incidence of cracking was not significant between the New and the BG groups because the gloves from the BG group were in the best condition (Chapter Four, 4.3). Cracks were a very a striking characteristic in the forty-eight hour immersion experiment occurring in both

unwashed samples and one washed sample. These findings suggest that Top Clip Blue Shield® caused cracking in PVC gloves, which supports the previous work of Canning (1995). Cracks were not a characteristic of the other immersion experiments and this suggests that a particular solvent or another ingredient of Top Clip Blue Shield® was responsible for causing cracking. The other possibility is that there may have been some interaction between the interior surface and the exterior surface that could have enhanced permeation, and which may have given rise to swelling, followed by contraction during drying and hence crack development.

Smooth areas were primarily observed on new glove samples in all the immersion experiments, and therefore they must be related to the manufacturing process. Smooth areas were a significant characteristic of the washed glove samples in the both surfaces immersion experiments but only at thirty-six hours. It may be that smooth areas are a product of the permeation process and that the smoothness may be the top or plateau region of a convexity, as in some cases the boundaries between defects were indistinct.

5.4.2 Nitrile-butadiene rubber gloves

There were two types of NBR gloves collected from TF, MSA™ and Sol-Vex™. These gloves had similar working life histories and therefore it was only possible to compare types. The NBR gloves in the immersion tests were Sol-Vex™ as this was the most commonly used glove.

There were more cavities in the used NBR gloves compared to their new counterparts, but not at significant levels. Although there were significant differences between both the new and used MSA™ and the used Sol-Vex™, this implies that cavities are the product of the manufacturing process for MSA™ gloves but not Sol-Vex™ rather than a defect caused from use. The MSA™ gloves have a more textured surface on the predetermined sampling areas. In both of the immersion tests, cavities were not a significant finding, and therefore, exposure to Top Clip Blue Shield®, Jetdip® and Lorsban® did not cause cavities. In the one minute immersion experiments cavities were a significant finding for the Lorsban® test. This finding was unexpected and cannot be explained in light of the other findings.

There were fewer contaminants on the NBR gloves compared to the PVC. The NBR gloves are much less textured than the PVC and are not tacky, and therefore it would be more difficult for substances to affix to them. There were differences between the groups and this maybe due to the slightly more textured surface of the MSA™ gloves. In the both surfaces immersion experiments, there was a general trend for more

contaminants to reside on the unwashed gloves. This is more than likely due to the viscosity of the Top Clip Blue Shield® causing a film on the NBR where the contaminants may be retained. In the external surface immersion experiments, there were very few contaminants and these were confined to the treated samples, in particular, those exposed to the concentrated formulations. Again it is likely that the viscosity of the formulations enhanced the affixation of particulates. It was demonstrated that the cleansing method was effective for laboratory conditions. Contaminants were not a significant feature of the one minute immersion experiments, as was anticipated with the lack of air turbulence during the drying time.

Convexities were predominantly a feature of the new gloves and were therefore associated with the manufacturing processes. The used MSA™ gloves retained some convexities, but the Sol-Vex™ ones did not. This is similar to the PVC result and a similar conclusion may be determined. In the both surfaces immersion experiments, the new Sol-Vex™ did have some convexities and there were more of them in the unwashed samples, but this was not incremental over time. There was no clear cut pattern for convexities in the external surface immersion experiments. In the one minute immersion experiments, the Lorsban® samples had significantly more convexities. It seems likely that some convexities are caused by the manufacturing processes and others are due to exposure to OPs.

There were no differences in the number of cracks between the new types of gloves, although there were significant differences between the new Sol-Vex™ and both the new and used MSA™, with the used MSA™ having the greater quantities. It is, of course, not possible to ascertain the cause of the cracks in used gloves other than to assume that working conditions were related to cracking. In the twenty-four and thirty-six hour immersion experiments, cracks were more common in the washed samples. In the external surfaces immersion experiment cracks were a distinguishing phenomenon of all the treated samples. Overall, there were slightly more cracks in the diluted samples. A possible explanation for this is that polymers frequently absorb water leading to swollen convexities which contract during the drying out process and thus lead to crack formation. In the forty-eight hour both surfaces immersion experiment, cracks were greater in the unwashed samples. This may be related to absorption of the pesticide and the more severe cracking occurring during the drying out period as the solvents volatilised and the material shrank. In the one minute immersion experiments cracks were not a significant feature, and therefore, it can be assumed that this exposure is too short to propagate cracks.

Crazing was not a characteristic of any of the immersion experiments. The used Sol-Vex™ gloves were the only type of CPGs to exhibit crazing. This may have been due to weathering and/or their cleaning procedures, which involved being washed in a washing machine with water and detergent. Although crazing cannot be regarded as true material failure, it can lead to the propagation of larger cracks.

Slumps were primarily a characteristic of new Sol-Vex™, but only in the both surfaces immersion experiments, and are most likely a result of the dipping and drying process. This finding provides an indication that there are marked differences between batches.

5.4.3 Natural rubber gloves

Hy-Care™ and washing-up gloves were combined to form the NR group. The Hy-Care™ gloves were highly textured and both types were much more textured than the PVC or NBR gloves.

There were no differences between the number of cavities in the new and used washing-up gloves. The new NR only differed from one of the used groups and therefore it cannot be concluded that cavities are a result of working conditions, and this is confounded by the highly textured surface of the NR gloves, which makes observation difficult.

The intensely textured surface of the NR gloves allowed the retainment of contaminants. The washing-up gloves had few contaminants on them, as expected. It is interesting to note that the TF group had been washed in water and detergent, and therefore, it was expected that most of the contaminants would have been effectively removed which indeed was not the case as this group had the greatest amount of contaminants.

Convexities followed a similar pattern to the NBR and PVC gloves because there were more convexities on both types of new gloves compared to the used ones. The greatest frequency of convexities was found on the new washing up gloves and there were significant differences between the new and used washing up gloves. In this case, it is a reflection of the highly textured surface of the NR.

Most of the cracks were found in the used NR gloves from the OR group and none in the new gloves. Agricultural working conditions were responsible for cracking of NR gloves.

5.4.4 Polyvinyl chloride/nitrile butadiene rubber gloves

These gloves were extremely textured and the surface resembled that of a block co-polymer (Figure 5.2).

There were fewer cavities in the palmar surface of these gloves compared to the dorsal surface, with the exception of New 2. The most likely explanation is that these gloves were very soiled and the cavities in the palmar surface were filled and compacted due to pressure applied on the palmar surface during tasks, *e.g.* opening a drum.

Contaminants were much less on the new gloves. The used gloves were five years old, had been kept on the floor of the tractor and had never been washed. Consequently, a high degree of contamination was expected. Also the gloves were discoloured yellow, due to Stomp® according to the owner, and that the rough surface may contain contaminants. However, this was not the case as there were only significant differences between the New groups and V2. This is a puzzling result and would require much more dedicated experimentation to ascertain the cause. Given that there was only one pair of this type of gloves in the exchange program this was beyond the scope of this research.

Convexities in the PVC/NBR gloves deviated from the pattern in the PVC, NBR and NR gloves because there were fewer in New 2 and more in New 1 than the used gloves. However, there were fewer in the palmar samples which may indicate that some of the convexities had worn off, although there were no significant differences between New 1 and the used gloves. This, of course, may have been different if there had been a larger sample size to draw upon.

The smooth areas were only observed on New 2. Determination of smooth areas on the PVC/NBR was rather difficult to determine because of the large size of the integral structures. The smooth areas may be spaces between the structures rather than a product from environmental agents. Again it is not possible to make a firm conclusion due to the small sample size.

5.4.5 Thin polyvinyl chloride gloves

These unidentified gloves were discoloured and dirty, and therefore, it was not surprising to find that they harboured many contaminants. Cavities were the major defect found in these gloves, followed by convexities and cracks. Of course it is not possible to draw any firm conclusions from these gloves because they could not be compared with new ones. However, it does seem likely that these gloves are not robust enough or suitable for CPGs or general farm-work.

5.5 Chapter Summary And Conclusion

The type of defects that occur on new and used agricultural CPGs has been ascertained and in the process a novel method for describing the defects on new and used CPGs has been developed. This work is complementary to other methods of CPG testing and provides new knowledge about the flaws in the materials that are a result of the manufacturing processes and those that occur from agricultural use. This method can only be semi-quantitative because it was impossible to assess the area, which is the main limitation, as the size of the defects cannot be measured. It may be that the larger the defect the greater the risk of potential dermal exposure but that would require strength testing, defect identification and measurements in combination with degradation and permeation testing and is beyond the scope of this research. It is therefore recommended that such research be instigated.

The most widely used gloves were PVC. Many of these presented with defects in the new gloves, which can only contribute to their early failure. Significant defects that were found on the PVC gloves were cavities, cracks and convexities. The immersion experiments provided interesting results. The extensive permeation of Lorsban® through the PVC fingers is rather alarming and it is therefore recommended that PVC gloves not be used for the application or mixing of Lorsban®. Physical defects can be caused by exposure to formulated OPs even after one minute. The sample sizes of the one minute immersion experiments were small and it may be beneficial to repeat these experiments.

The NBR gloves were only from the TF group and again there were a range of defects. Defects that were exclusive to these gloves were slumps and crazes.

The less numerous groups included the NR, thin PVC and the PVC/NBR. The NR gloves were highly textured and contained cracks, cavities and convexities. Most people used the Hy-Care™ because of the fit, increased tactility and grip function (Chapter Four, 4.3.3). However, because of the type of defects that were revealed they are not suitable for CPGs or general farm work. The same factors apply to the washing up gloves. The unidentified thin PVC gloves, which were in poor condition, had an abundance of cavities and were heavily soiled. From these observations they cannot be deemed suitable for CPGs or general farm work. The PVC/NBR were very robust and seemed to be the most superior type of glove presented in this study. The used gloves were five years old and were poorly cared for, but they had no cracks and few other defects. It was unfortunate that only one pair of this type of gloves could be collected.

It was not possible to determine if the maintenance factors had an impact on the type or frequency of the defects. This will require controlled laboratory experiments. However, the important finding in this work was that most of the gloves were two years old and that there was not a consistent pattern to their cleaning. Storage ranged from good to poor and was generally haphazard.

Exposure to the external surfaces is more likely to be representative of field conditions. Nevertheless spills can and do occur down the inside of gloves particularly when the gloves are worn outside coveralls, as discussed in Chapter Three (3.8.5).

This chapter has identified and described physical defects on the surface of several types of new and used CPGs that have been exposed to various working conditions and OPs. The chemical responses are described in the next chapter.

Chapter Six

Chemical Analyses Of New And Used Chemically Protective Gloves By X-Ray Energy Dispersive And Gas Chromatography And Mass Spectroscopies

6.1 Introduction

Chemical analyses of the external and interior surfaces of CPGs provide valuable information about their composition and the substances to which have been exposed. While X-ray microanalysis is a widely used technique to determine the elemental composition of many materials, it has not previously been used on CPGs.

Two types of chemical analyses were conducted on the same CPGs described in Chapter Five (5.2). Techniques for X-ray microanalysis and gas chromatography (GC) and mass spectrometry (MS) are described next.

6.1.2 X-ray microanalysis

The basis of X-ray microanalysis involves the identification of X-ray lines emitted by the specimen under the electron beam. The X-ray energy spectrum provides qualitative information about the presence of particular elements. Quantitative data are determined by the counts per second (cps), which demonstrate the concentration of the element under the peak. The spectrum plots the number of X-rays on the vertical axis and the energy on the horizontal axis. Scholarly discussion involving the theory of X-ray microanalysis is provided by Reed (1975) and Reimer (1985, pp.365–401).

The background radiation is that part of the signal that is not due to line emission, which is distinct from the continuous background radiation or bremsstrahlung. The background radiation is caused when the beam electrons decelerate in the coulombic fields of the atoms (Blok-van Hoek and Pinxter 1993, pp.3–4).

Energy dispersive spectroscopy (EDS) and wavelength-dispersive spectroscopy (WDS) are common X-ray analytical methods. The main advantages of EDS over WDS methods are that only one detector is required, it is capable of rapid analysis and simultaneous detection and with a Super Atmospheric Thin Window (SATW) can analyse all elements heavier than boron. There are some disadvantages, such as an increased background reading from back scattered electrons and occasional peak overlap will occur (Blok-van Hoek and Pinxter 1993, p.15; Sawyer and Grubb 1987, p.34; Reimer 1985, pp.365–393). Elemental analysis was done with EDS in the experiments in this chapter. It must be pointed out that the peaks identify the elements that may be part of various compounds, *e.g.* silicon may be part of silicon dioxide and aluminium may be part of alumina.

6.1.3 Gas chromatography and mass spectrometry

Chromatography is an analytical method where the flow of a solvent or gas ameliorates the partitioning of substances by a differential migration in a porous sorptive medium in a narrow initial zone (Heftman 1967, p.15). The partitioning of components within a mixture occurs between two different phases; one mobile and one stationary. Each compound in a mixture partitions at a different degree between the two phases, which is related to their solubility in each phase.

Gas chromatography is a specific form of chromatography where the mobile phase is an inert carrier gas and the stationary phase is a high molecular weight liquid. This liquid is deposited on the walls of a long capillary tube or on finely divided particles. The inert gases are usually nitrogen, hydrogen, helium and argon. The gas that is used is directed to flow into a temperature controlled sample injection apparatus. Samples are injected into the carrier gas through an injection port that is connected to a GC column. A detector is attached to the exit of the column, which identifies components as they are eluted. A chromatogram is produced that shows the analytical data, the peak providing qualitative data and the area under the peak depicting quantitative data.

Mass spectrometry is a method used to study the masses of atoms. It involves the production of ions, mass separation and recording of the ions that have been formed. There are many techniques for ionisation, mass separation and recording. A sample in the gaseous state is bombarded with electrons that generates organic ions from collisions (Karasek and Clement 1988, p.14; Pecsok *et al.* 1976, pp.316–320). These organic ions are unstable and form radicals and other ions. The breakup pattern of molecules or ions is dependent upon the functional groups and the carbon skeleton. Consequently, a fragment's structure and mass can give information about the structure of the parent molecule. Typically it is the positively charged fragments that are detected. The mass spectrum is a plot of the abundance of the ions versus the mass to charge ratio (m/z). This spectrum can also be seen as "a record of particle mass versus relative abundance of the particles" (Fessenden and Fessenden 1990, p.873). The combination of GC-MS provides a powerful tool for separation and identification of components within complex mixtures.

6.1.4 Aims

The aims of this chapter are:

1. to determine by analysis, the elements on the surface of used CPGs and to compare them to the new CPGs, for the purpose of examining chemical evidence of degradation of the glove matrix;
2. to determine if there were any OP residues on the surface of used CPGs and those exposed to OPs in laboratory situations;
3. to determine if there were any pesticide residues in the lining of used PVC gloves; and
4. to determine if any of the defects acted as reservoirs for OPs.

6.2 Materials And Methods

The same samples were used as in Chapter Five (5.2), which included new gloves, used gloves and those used in the immersion experiments. Generally only every second specimen was subject to this type of analysis, or in other words one glove from each pair. The exceptions to this were that two of the thin PVC gloves were analysed, and, in the case of the PVC/NBR, all the new samples were analysed as were two used samples, including dorsal and ventral surfaces of the new and used gloves.

The ESEM 2020 was used, as described in Chapter Five (5.2.3), with a Link Pentafet SATW EDS and a long working distance gaseous secondary electron detector (GSED). To maintain consistency of the analytical results, the EDS was calibrated on pure copper to obtain 4000 cps at above analytical conditions, which involved both specimen vertical position and condenser setting adjustments. The standard acquisition time was set at sixty seconds. The operating conditions were: accelerating voltage of 10 kV; working pressure of 1.5 T and condenser of 45% to maximise the X-ray yield. Initially readings were taken to ascertain which elements were present on the surface of the gloves. These readings were done at a magnification of 1000 x. Following this, to maintain an effective comparison with the ESEM images (from Chapter Five), the magnification was maintained at 400 x.

To obtain the real area under the peak of interest the cursor was set on either side of the full width half maximum point under the peak. Other windows were set adjacent to the bases of the peaks to determine the background readings, which were subsequently subtracted from the peak of interest. This method resulted in some small negative readings, particularly for sulfur and phosphorus, which were interpreted as no excesses over the background reading and therefore were counted as zero readings. Three readings at different locations were taken from each sample after the surface

topography had been broadly scanned to ensure that a representative area would be analysed. The elements analysed were carbon, oxygen, aluminium, silicon and chlorine, which were the significant peaks. Phosphorus and sulfur were also analysed because they are constituents of many pesticides, in particular OPs.

The interior surface areas of some of the cracks in PVC gloves were analysed and compared to areas immediately outside the defects. Analyses within the defects were at different magnifications so that the surface area of the defect would fit into the scan window. Some of the contaminants were selected haphazardly and analysed at appropriate magnifications.

6.2.1 Gas chromatography/mass spectrometry

Pesticide contamination in the lining of the used PVC gloves was investigated by GC-MS methods. The middle finger was cut from two of the DP gloves (DP 1 and DP 6) and from two of the OR gloves (OR 1 and OR 13). These gloves had been used for a variety of chemicals (Table 4.8). One new glove was run as a control. Each finger was filled with distilled water to within 1 cm clearance from the top. Distilled water, rather than a solvent, was used to ensure minimal dissolution from the glove matrix. The glove finger was then pegged to a wire suspended across a sonicator filled with distilled water so that most of the finger was submerged, but there was no possibility of the internal and external water being exchanged. The finger was then ultrasonicated (50/60 Hz) for five minutes. A new pipette was used for each specimen to transfer the internal fluid to dedicated glass vials.

Gas chromatography (HP5890), mass spectrometry (HP5970B) was used with a 25 m x 0.32 internal diameter column with helium as the carrier gas. The GC oven temperature ranged from 60°C to 150°C at 30°C per minute to 290°C at ten minutes. The MS scan conditions were m/z 40–550, with 1.2 scans per second. Chemostation™ software was used. Chloroform was used in the extraction process and 1 mL was placed in each vial for two hours and then 1 µL was injected into the GC.

6.2.2 Statistical analyses

The data were grouped into their respective polymer or elastomer families and then subdivided according to their origin or make. None of the groups of gloves were similar and therefore the data were not aggregated, as in Chapter Five. The data for the dorsal and ventral surfaces of PVC/NBR gloves were grouped together. The data were checked for normal distribution (Kolmogorov-Smirnov Test) and equal variances (Levene Median Test). The types of elements analysed in each type of glove material

were investigated with Kruskal-Wallis one way ANOVA on Ranks or One Way ANOVA, depending upon whether the data were normally distributed or not. Where the sample sizes were unequal, the results of all the pairwise multiple comparisons tests were determined by Dunn's Test, and where they were equal Student-Newman-Keuls method was used. In the smaller experiments with only two groups for comparison a t test was conducted on those with normal distribution and a Mann-Whitey Rank Sum Test for those not normally distributed. The thin PVC gloves were analysed with descriptive statistics as they had no comparative group. The statistical program Sigmastat™ was used for all of these analyses.

6.3 Results

The results from the exchange program are detailed first in the following order PVC, black PVC, NBR (Sol-Vex™ followed by MSA™), NR (Hy-Care™ followed by washing-up), PVC/NBR and finally the thin PVC. This section is followed by the immersion experiments, PVC precedes NBR. The GC-MS results follow the PVC immersion experiments. Finally the chemical analyses of the physical defects and contaminants are given.

6.3.1 Gloves in field use

6.3.1.1 Polyvinyl chloride gloves

6.3.1.1.1 *Red polyvinyl chloride gloves*

The amount of carbon on PVC gloves differed markedly between origins ($H = 43$, d.f. $= 4$, $P < 0.0001$). Oxygen concentrations also contrasted strongly between origins ($H = 46.6$, d.f. $= 4$, $P < 0.0001$). Aluminium and silicon concentrations differed between origins ($H = 30.1$, d.f. $= 4$, $P < 0.0001$ and $H = 31.4$, d.f. $= 4$, $P < 0.0001$) respectively. There were marked variations for phosphorus concentrations ($H = 25.6$, d.f. $= 4$, $P = < 0.0001$). The concentrations of sulfur varied considerably between origins ($H = 40.2$, d.f. $= 4$, $P < 0.0001$) as did chlorine ($H = 30.8$, d.f. $= 4$, $P < 0.0001$). The elements from the various origins are depicted in Tables 6.1 and 6.2. Figure 6.1 shows the comparative spectra.

TABLE 6.1

Elements as analysed by EDS (counts per second) on the surface of PVC gloves from various origins. The median, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Elements	Origins	n	Median	25%	75%
Carbon	New	12	6412	4358	7194
	BG	3	410	330	443
	DP	15	830	620	880
	OR	24	677	500	1006
	TF	27	458	384	508
Oxygen	New	12	6071	4603	6925
	BG	3	1231	983	1365
	DP	15	3482	2064	4253
	OR	24	2278	1408	3178
	TF	27	1105	978	1447
Aluminium	New	12	387	321	450
	BG	3	95	83	127
	DP	15	610	235	820
	OR	24	358	177	463
	TF	27	145	124	196
Silicon	New	12	535	427	566
	BG	3	192	154	233
	DP	15	1604	562	2460
	OR	24	848	562	1958
	TF	27	336	259	443
Phosphorus	New	12	0	0	0
	BG	3	7	2	18
	DP	15	76	8	101
	OR	24	10	0	39
	TF	27	0	0	10
Sulfur	New	12	391	333	456
	BG	3	69	61	88
	DP	15	180	71	224
	OR	24	351	167	611
	TF	27	83	64	124
Chlorine	New	12	30375	30055	32130
	BG	3	3080	2758	3350
	DP	15	3513	2702	5174
	OR	24	3299	1759	8740
	TF	27	3699	3118	4167

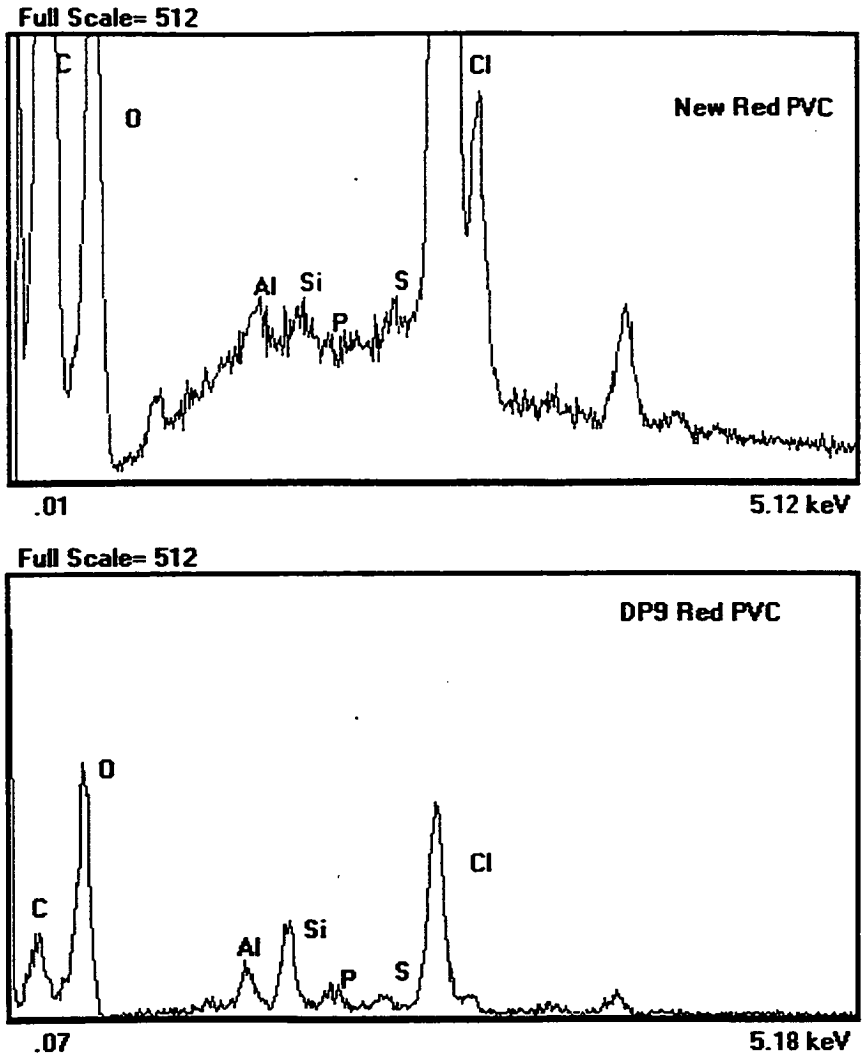
TABLE 6.2

Comparison of the main elements (counts per second) detected on PVC gloves from various origins (Dunn's method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		**Origins**				
		New	BG	DP	OR	TF
Carbon	New					
	BG	<0.05				
	DP	<0.05	NS			
	OR	<0.05	NS	NS		
	TF	<0.05	NS	NS	NS	
Oxygen	New					
	BG	<0.05				
	DP	NS	NS			
	OR	<0.05	NS	NS		
	TF	<0.05	NS	NS	NS	
Aluminium	New					
	BG	<0.05				
	DP	NS	<0.05			
	OR	NS	NS	NS		
	TF	<0.05	NS	<0.05	NS	
Silicon	New					
	BG	NS				
	DP	NS	<0.05			
	OR	NS	<0.05	NS		
	TF	NS	NS	<0.05	<0.05	
Phosphorus	New					
	BG	NS				
	DP	<0.05	NS			
	OR	<0.05	NS	NS		
	TF	NS	NS	<0.05	NS	
Sulfur	New					
	BG	<0.05				
	DP	<0.05	NS			
	OR	NS	NS	NS		
	TF	<0.05	NS	NS	NS	
Chlorine	New					
	BG	<0.05				
	DP	<0.05	NS			
	OR	<0.05	NS	NS		
	TF	<0.05	NS	NS	NS	

FIGURE 6.1

X-ray microanalysis spectrum of a new red PVC glove compared to one from the field



6.3.1.1.2 *Black polyvinyl chloride gloves*

New black PVC gloves were compared to the used black PVC from the BG group. All the elements except chlorine passed the normality test. There were marked differences for carbon between the two ($t = 10.8$, d.f. = 13, $P < 0.0001$). Oxygen concentrations were not the same ($t = 2.81$, d.f. = 13, $P = 0.0146$). There were no differences for aluminium between the two groups ($t = -0.657$, d.f. = 13, $P = 0.5225$ with a 95% confidence interval of –964.6 to 514.6). However, it should be noted that the power of this test was executed below the desired power, and therefore these results invite caution. Similar results were obtained for silicon ($t = 0.941$, d.f. = 13, $P = 0.3640$ with a 95% confidence interval of –115 to 292). Again the power of the performed test was low. Phosphorus did not vary between the groups ($t = -1.66$, d.f. = 13, $P = 0.1213$ with a 95% confidence interval of –124.6 to 16). As in the previous two cases the power of the test was conducted at below the optimal power. There were differences for sulfur concentrations between the groups ($t = 6.55$, d.f. = 13, $P < 0.0001$). Chlorine differed between the two groups ($T = 6$, $P = 0.0115$). The results are presented in Table 6.3 and Figure 6.2.

TABLE 6.3

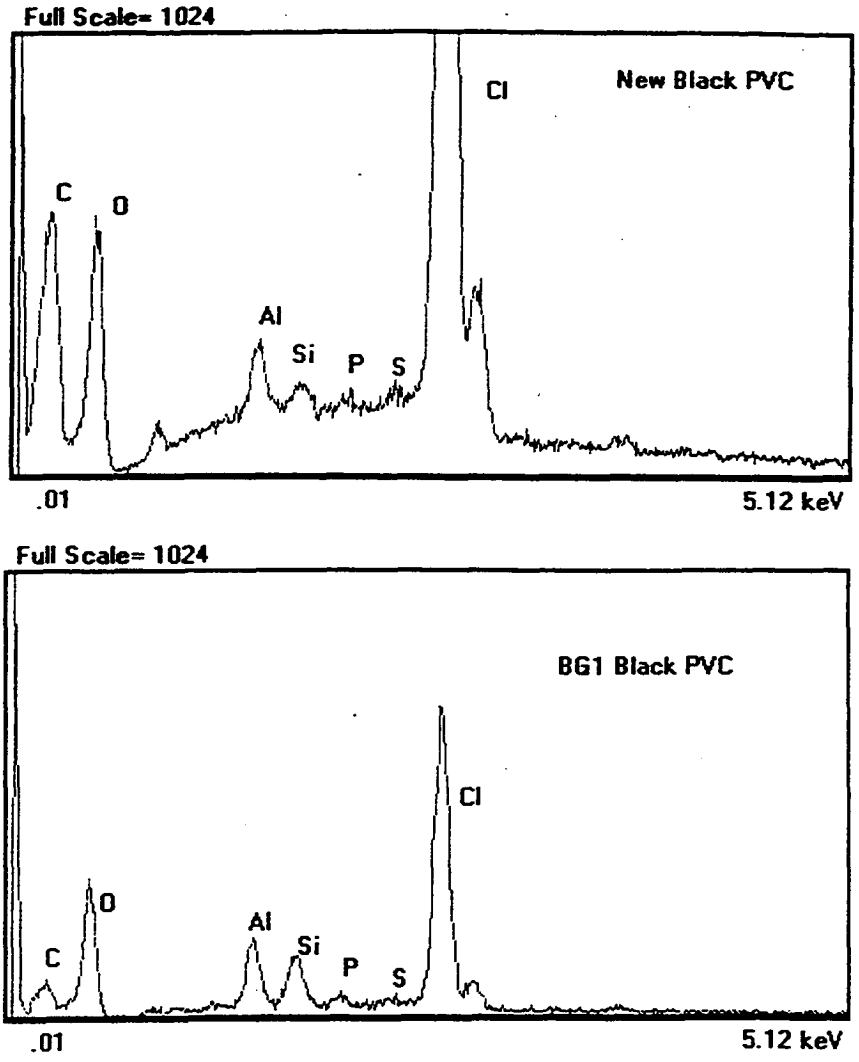
Elements as analysed by EDS (counts per second) on new and used black PVC gloves. The means ± standard errors and their differences (t test) are shown. Chlorine has the medians, 25th and 75th percentiles shown (Mann-Whitney Rank Sum Test).

Elements	Glove	n	Mean ± se	Differences of the means
Carbon	New	12	4309 ±171	3802
	BG	3	507 ± 46	
Oxygen	New	12	4038 ± 362	2104
	BG	3	1934 ± 177	
Aluminium	New	12	796 ± 166	–225
	BG	3	1021 ± 81	
Silicon	New	12	855 ± 43	89
	BG	3	766 ± 70	
Phosphorus	New	12	75 ± 15	–54
	BG	3	129 ± 26	
Sulfur	New	12	297 ± 15	7
	BG	3	97 ± 6	

			Median	25%	75%
Chlorine	New	12	33918	31471	38945
	BG	3	3922	3374	3922

FIGURE 6.2

X-ray microanalysis spectrum of a new black PVC glove compared to one from the field



6.3.1.2 Nitrile-butadiene rubber gloves

The two types of NBR gloves, Sol-Vex™ and MSA™ are detailed separately.

6.3.1.2.1 *Sol-Vex™ gloves*

All the data for the new and used Sol-Vex™ samples failed the normality tests. Carbon concentrations differed markedly between the two groups (T = 110, P <0.0001), as did oxygen (T = 110, P <0.0001). Aluminium also differed between the two, although not quite as strongly (T = 108, P = 0.0012). There was a considerable difference for silicon (T = 110, P <0.0001). Phosphorus did not vary between the two groups (T = 57, P = 0.502). There were distinctive differences for sulfur and chlorine between the two groups (T = 110, P <0.0001 in both cases). Table 6.4 portrays the results. Comparative spectra are given in Figure 6.3.

TABLE 6.4

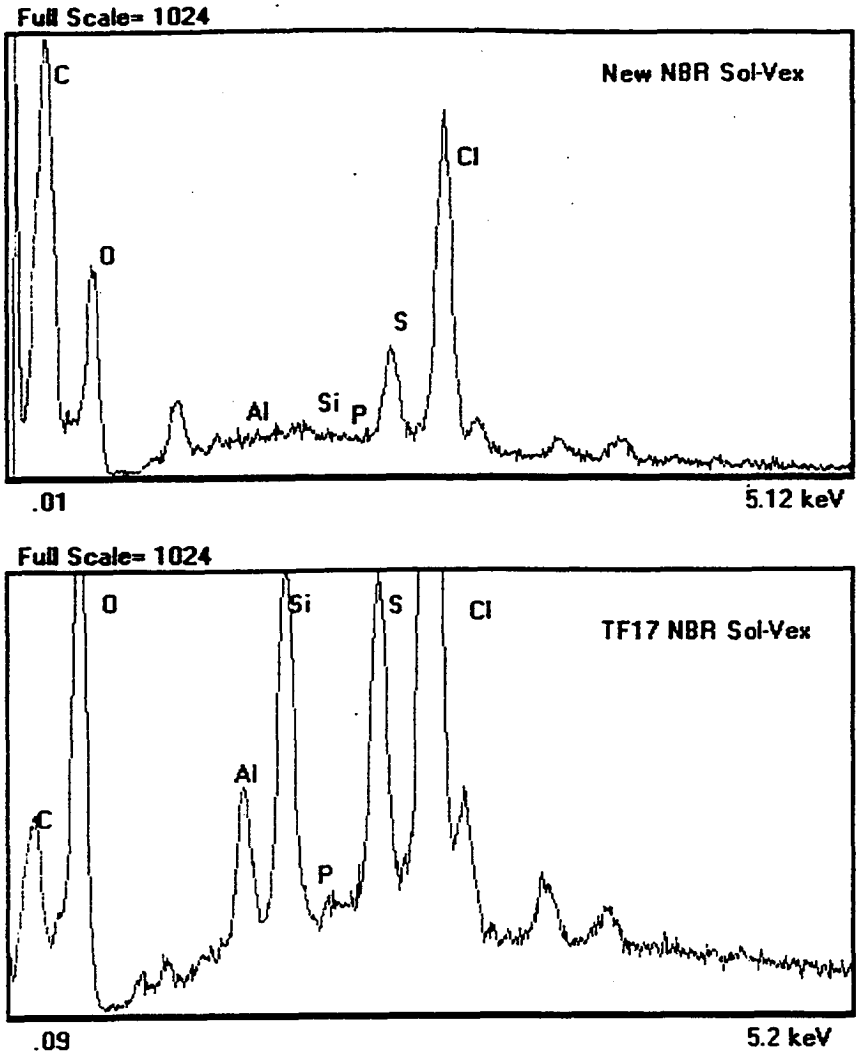
Elements as analysed by EDS (counts per second) on new and used (TF) Sol-Vex™ gloves. The medians, 25th and 75th percentiles are shown (Mann-Whitney Rank Sum Test).

Elements	Glove	n	Median	25%	75%
Carbon	New	6	3963	3721	4205
	TF	15	141	119	334
Oxygen	New	6	7023	6873	8877
	TF	15	290	232	504
Aluminium	New	6	311	228	1724
	TF	15	40	29	82
Silicon	New	6	1003	942	1063
	TF	15	83	42	189
Phosphorus*	New	6	0	0	0
	TF	15	0	0	0
Sulfur	New	6	3518	3018	4026
	TF	15	123	57	179
Chlorine	New	6	29639	29596	31379
	TF	15	486	317	851

* The mean for phosphorus = 0.77

FIGURE 6.3

X-ray microanalysis spectrum of a new Sol-Vex™ glove compared to one from the field



6.3.1.2.2 *MSA™ gloves*

All the data for the concentrations of the elements on the MSA™ gloves failed the normality tests, except for aluminium. Carbon, oxygen, silicon, phosphorus, sulfur and chlorine concentrations differed strongly between the two groups ($T = 126$, $P < 0.0001$ for all). Aluminium varied between the two. However, the power of the performed test was below the optimum power and therefore this result invites cautious interpretation ($t = 2.16$, d.f. = 16, $P = 0.0460$). The data are summarised in Table 6.5 and the spectra in Figure 6.4.

TABLE 6.5

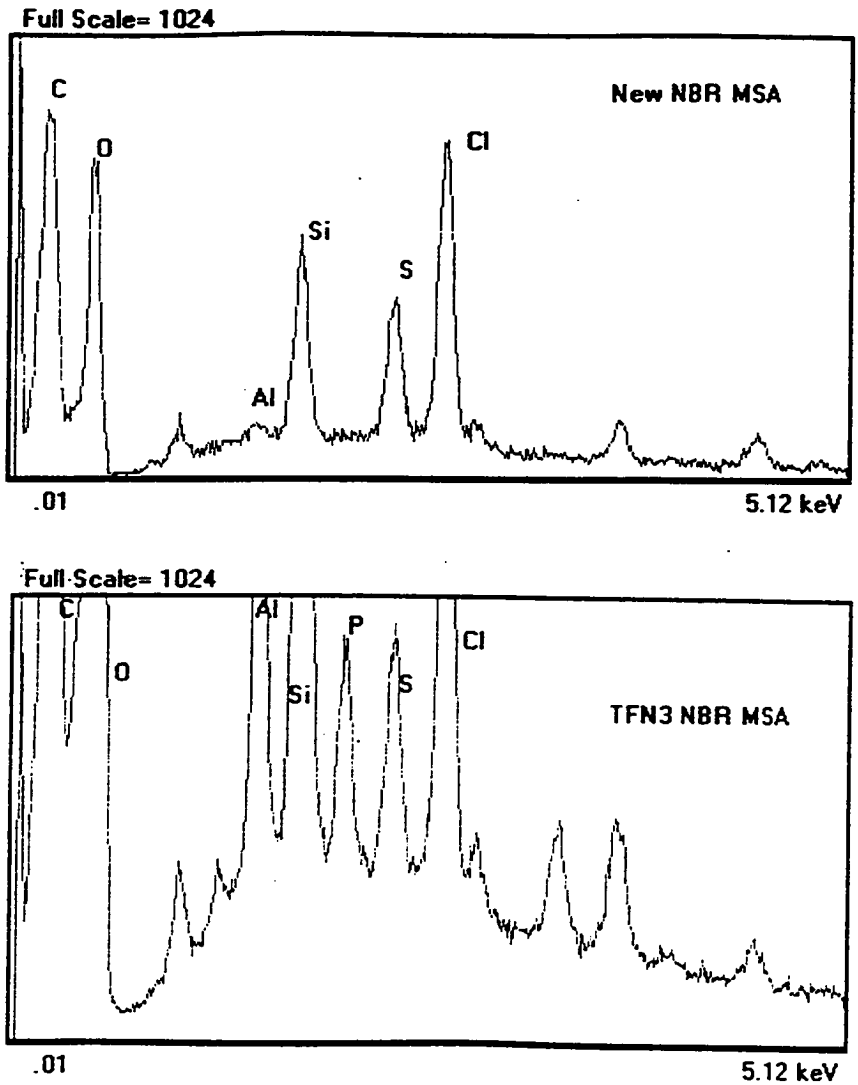
Elements as analysed by EDS (counts per second) on new and used MSA™ gloves. The medians, 25th and 75th percentiles shown (Mann-Whitney Rank Sum Test) for the abnormal distributions. The means ± standard errors and the difference of the mean are shown (t test) for aluminium.

Elements	Glove	n	Median	25%	75%
Carbon	New	9	4703	2921	6732
	TF	9	150	103	202
Oxygen	New	9	3872	2251	5249
	TF	9	438	389	686
Silicon	New	9	3347	1708	4054
	TF	9	257	191	371
Phosphorus	New	9	0	0	0
	TF	9	5	3	40
Sulfur	New	9	2659	2135	3153
	TF	9	61	46	93
Chlorine	New	9	5888	3794	6317
	TF	9	239	148	513

			Mean ± se	Difference of the mean
Aluminium	New	9	187 ± 33	76
	TF	9	111 ± 12	

FIGURE 6.4

X-ray microanalysis spectrum of a new NBR (MSA) glove compared to one from the field



6.3.1.3 Natural rubber gloves

There were two types of natural rubber gloves, the Hy-Care™ gloves from the TF and the OR groups, and the washing-up gloves, which were only from the BG group.

6.3.1.3.1 *Hy-Care™ gloves*

All the data for the concentrations of the elements failed the normality tests with the exception of oxygen. There were no differences for carbon ($H = 2.23$, d.f. = 2, $P = 0.327$). Mean oxygen concentrations differed significantly between origins ($F_{2,12} = 19.3$, $P = 0.0002$). There were variations in aluminium concentrations between origins ($H = 6.90$, d.f. = 2, $P = 0.0317$). Silicon varied between origins ($H = 11$, d.f. = 2, $P = 0.0040$). The concentrations of phosphorus differed between origins ($H = 7.76$, d.f. = 2, $P = 0.0206$). Sulfur concentrations did not vary between origins ($H = 2.03$, d.f. = 2, $P = 0.363$). Chlorine differed between origins ($H = 10.8$, d.f. = 2, $P = 0.0046$). The data are summarised in Tables 6.6 and 6.7 and the spectra are presented in Figure 6.5.

TABLE 6.6

Elements as analysed by EDS (counts per second) on the surface of Hy-Care™ gloves from various origins. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks). The means ± standard errors are shown for oxygen (One Way ANOVA).

Elements	Origins	n	Median	25%	75%
Carbon	New	6	1853	684	9228
	OR	6	1158	1120	1335
	TF	3	860	613	1017
Aluminium	New	6	974	287	1658
	OR	6	665	446	1012
	TF	3	92	66	116
Silicon	New	6	70	15	169
	OR	6	2015	1372	2709
	TF	3	307	258	349
Phosphorus	New	6	4	0	13
	OR	6	109	59	136
	TF	3	0	0	9
Sulfur	New	6	318	58	881
	OR	6	230	196	233
	TF	3	131	104	154
Chlorine	New	6	23	16	33
	OR	6	141	97	194
	TF	3	15	5	20
				Mean ± se	
Oxygen	New	6		1174 ± 353	
	OR	6		3480 ± 357	
	TF	3		455 ± 58	

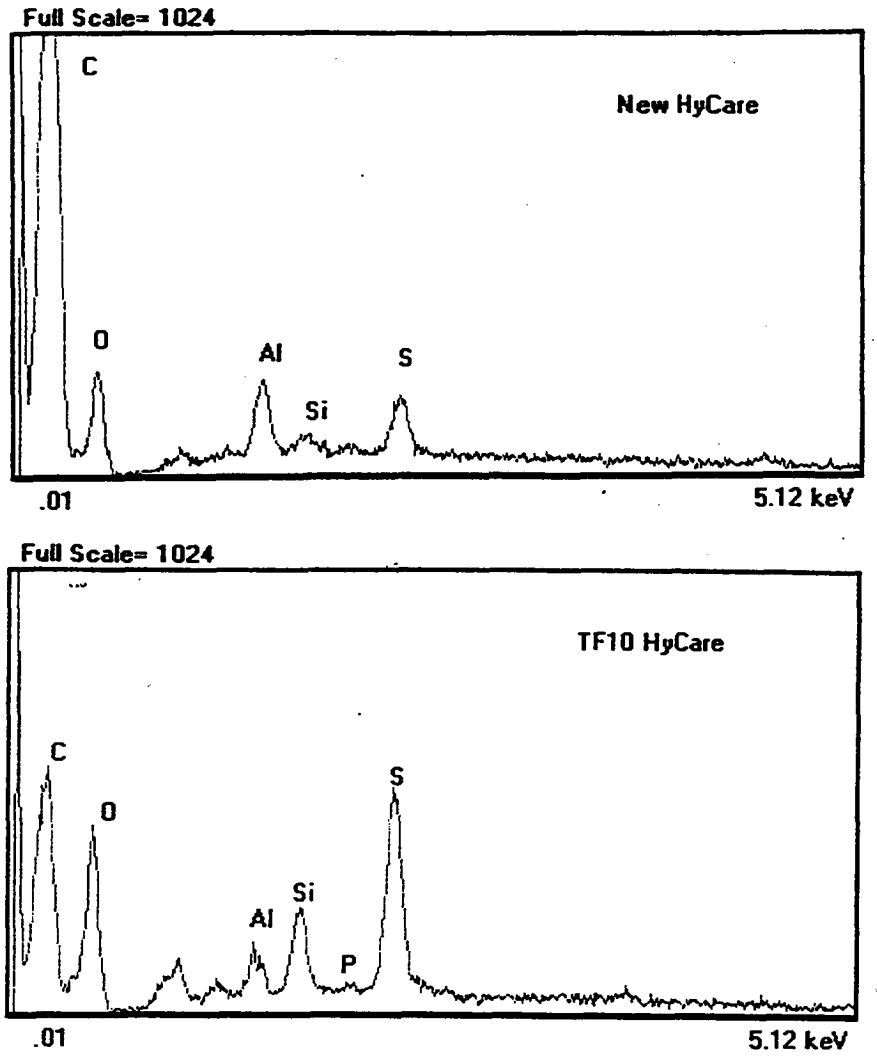
TABLE 6.7

Comparison of the elements (counts per second) detected on Hy-Care™ gloves from various origins (Dunn's method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		Origins		
		New	OR	TF
Oxygen	New			
	OR	<0.05		
	TF	NS	<0.05	
Aluminium	New			
	OR	NS		
	TF	<0.05	NS	
Silicon	New			
	OR	<0.05		
	TF	NS	NS	
Phosphorus	New			
	OR	NS		
	TF	NS	NS	
Chlorine	New			
	OR	<0.05		
	TF	<0.05	NS	

FIGURE 6.5

X-ray microanalysis spectrum of a new Hy-Care™ glove compared to one from the field



6.3.1.3.2 *Washing-up gloves*

Both used gloves were analysed in this section as the material was very sensitive to the beam. The data for carbon and oxygen concentrations were the only two to pass the normality tests and fail the equal variance tests. Chlorine passed both of these tests. There were no differences for the concentrations of carbon between the groups (T = 57, P = 0.963). Oxygen differed between the groups (T = 3.10, P = 0.0169). Aluminium did not differ between groups (T = 64, P = 0.542). Silicon varied between groups (T = 23, P = 0.0017). There were differences for phosphorus concentrations between the groups (T = 87, P = 0.0053). Sulfur did not vary between the groups (T = 51, P = 0.606). There were differences for chlorine concentrations between the two groups (t = 2.88, d.f. = 16, P = 0.0108). However, this test was conducted at slightly beneath the desired power, and therefore caution is required when interpreting this result. The results are presented in Table 6.8 and comparative spectra in Figure 6.6.

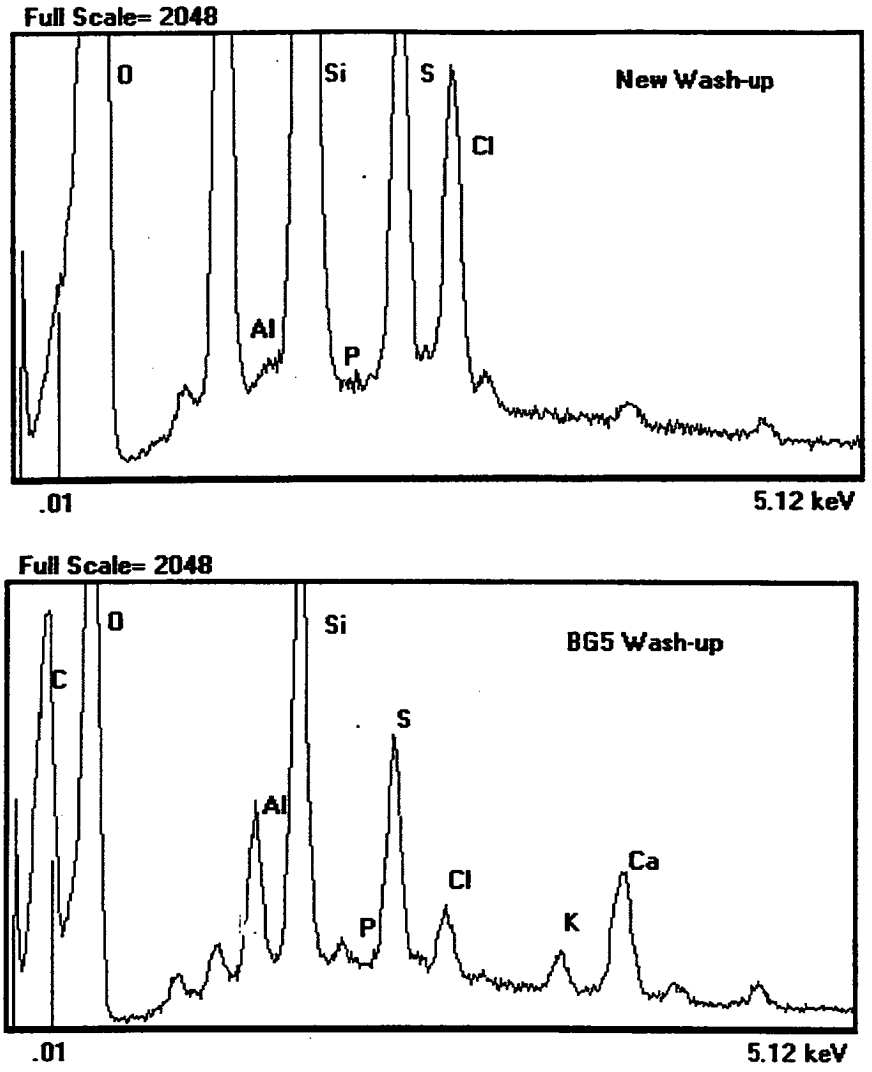
TABLE 6.8

Elements as analysed by EDS (counts per second) on new and used washing-up gloves. The medians, 25th and 75th percentiles are shown (Mann-Whitney Rank Sum Test). The means ± standard errors and the differences of the mean are shown (t test) for chlorine.

Elements	Glove	n	Median	25%	75%
Carbon	New	12	3375	2668	4076
	BG	6	7582	579	16243
Oxygen	New	12	34542	29088	41903
	BG	6	15477	1982	29063
Aluminium	New	12	244	0	7231
	BG	6	1947	346	4248
Silicon	New	12	34038	24305	37164
	BG	6	6620	1214	14064
Phosphorus	New	12	0	0	0
	BG	6	34	12	54
Sulfur	New	12	6158	5144	7473
	BG	6	3973	552	7755
				Mean ± se	Difference of the mean
Chlorine	New	12		4884 ± 634	3058
	BG	6		1826 ± 794	

FIGURE 6.6

X-ray microanalysis spectrum of a new washing-up glove compared to one from the field



6.3.1.4 Polyvinyl chloride/nitrile-butadiene rubber gloves

Oxygen, silicon and phosphorus passed both the normality and equal variance tests. Carbon differed between the two groups ($T = 21$, $P < 0.0001$). There were variations in the concentrations of aluminium between the groups ($T = 82$, $P = 0.0218$). Sulfur differed between groups ($T = 31$, $P = 0.0269$) as did chlorine ($T = 22$, $P = 0.0012$). Silicon differed between groups ($t = -3.97$, d.f. = 16, $P = 0.0011$). Oxygen concentrations did not differ between groups ($t = -0.780$, d.f. = 16, $P = 0.4467$). There were no differences for phosphorus ($t = -1.56$, d.f. = 16, $P = 0.1388$). The oxygen and phosphorus tests were conducted below the desired power and caution is required to interpret these results. The data are summarised in Table 6.9 and spectra comparisons in Figure 6.7.

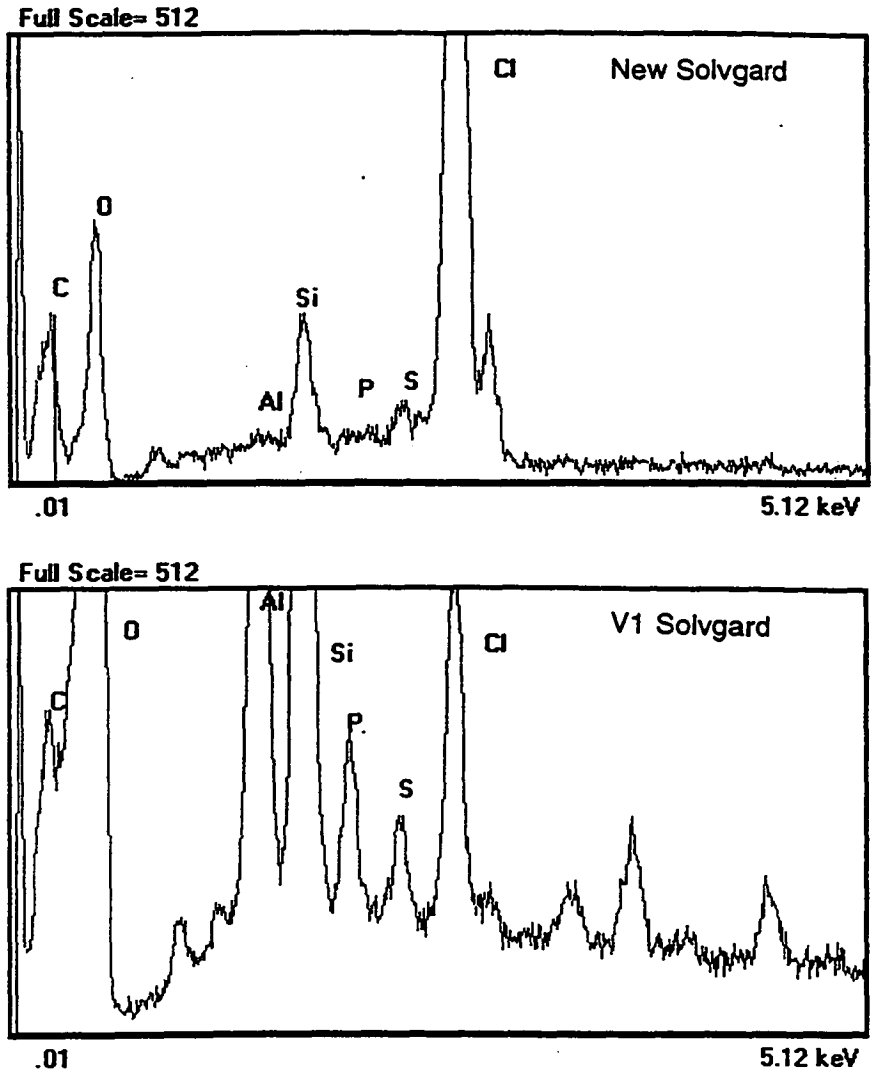
TABLE 6.9

Elements as analysed by EDS (counts per second) on new and used polyvinyl chloride/nitrile butadiene rubber gloves. The medians, 25th and 75th percentiles are shown (Mann-Whitney Rank Sum Test). The means ± standard errors and the differences of the means are shown (t test) for oxygen, silicon and phosphorus. V = used PVC/NBR gloves from a vegetable grower.

Elements	Glove	n	Median	25%	75%
Carbon	New	12	2641	1853	4430
	V	6	700	601	774
Aluminium	New	12	151	76	1683
	V	6	2197	1699	2223
Sulfur	New	12	473	323	731
	V	6	116	80	129
Chlorine	New	12	1713	9306	33900
	V	6	1018	716	2072
				Mean ± se	Differences of the means
Oxygen	New	12		3998 ± 478	−571
	V	6		4570 ± 370	
Silicon	New	12		1308 ± 129	−918
	V	6		2298 ± 202	
Phosphorus	New	12		143 ± 33	−83
	V	6		226 ± 35	

FIGURE 6.7

X-ray microanalysis spectrum of a new Solvgard™ glove compared to one from the field



6.3.1.5 Thin polyvinyl chloride gloves

These gloves could not be compared with new gloves and therefore descriptive statistics have been used and are presented in Table 6.10. A spectrum is illustrated in Figure 6.8.

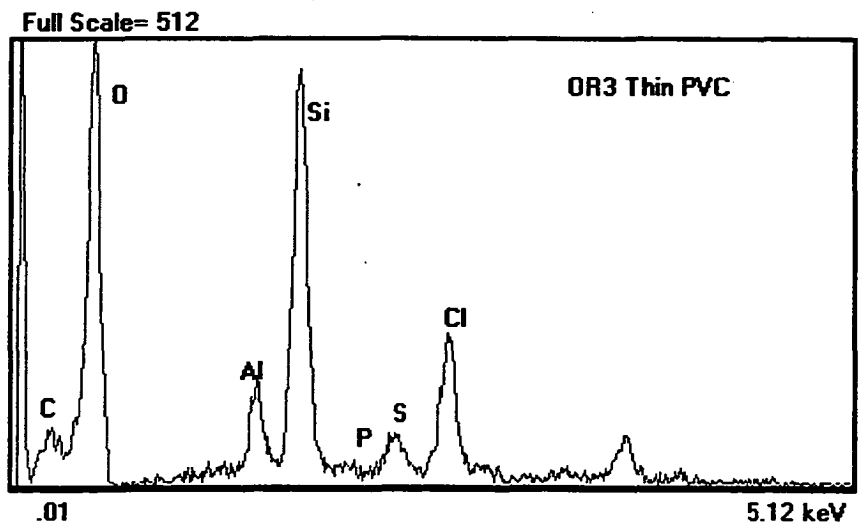
TABLE 6.10

Elements as analysed by EDS (counts per second) on the surface of used thin unsupported PVC gloves from the same orchardist (n = 6). The means and standard errors, medians, K-S distance and P values are shown.

Elements	Mean ± se	Median	25%	75%	K-S	P
Carbon	1315 ± 248	1111	8 01	1828	0.288	0.1257
Oxygen	5093 ± 996	3996	3383	8167	0.333	0.0358
Aluminium	1134 ± 297	1141	416	1785	0.97	0.5577
Silicon	2318 ± 358	2235	1563	2722	0.191	0.5909
Phosphorus	163 ± 87	81	0	276	0.234	0.3511
Sulfur	2130 ± 718	1798	580	3517	0.298	0.0989
Chlorine	15303 ± 1210	14558	12602	18035	91821	0.4517

FIGURE 6.8

X-ray microanalysis spectrum of a thin PVC glove from the field



6.3.2 Polyvinyl chloride gloves: immersion experiments

These experiments are presented in the following order: 1) immersions of the external surfaces (fingers) in Jetdip® and Lorsban®; 2) the one minute finger immersions in Jetdip® or Lorsban®; and 3) the immersion of both surfaces of PVC in Top Clip Blue Shield®.

6.3.2.1 Immersion of the external surfaces of polyvinyl chloride gloves in Jetdip®

The results of this group of experiments are subdivided into their three different time intervals.

6.3.2.1.1 *Polyvinyl chloride glove fingers immersed in Jetdip® for twenty-four hours*

Data for carbon, oxygen and aluminium concentrations passed the normality and equal variance tests. Carbon differed between treatments ($F_{2,9} = 12.3$, $P = 0.0027$). Differences for oxygen concentrations were observed ($F_{2,9} = 14$, $P = 0.0017$). There were also variations for aluminium ($F_{2,9} = 5.52$, $P = 0.0273$). This test was conducted below the optimum power and therefore interpretation requires caution. Silicon did not vary between treatments ($H = 1.96$, d.f. = 2, $P = 0.417$). Phosphorus differed between treatments ($H = 10$, d.f. = 2, $P = 0.0003$) as did sulfur ($H = 9.35$, d.f. = 2, $P = 0.0003$). The concentrations of chlorine varied between treatments ($H = 6.58$, d.f. = 2, $P = 0.0214$). The results are detailed in Tables 6.11 and 6.12.

TABLE 6.11

Elements as analysed by EDS (counts per second) on PVC glove fingers that had been immersed in concentrated or diluted Jetdip® for 24 hours. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks). The means ± standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Glove treatment	n	Median	25%	75%
Silicon	New	6	505	428	578
	Diluted	3	350	274	463
	Concentrated	3	491	488	498
Phosphorus	New	6	0	0	0
	Diluted	3	1109	904	1312
	Concentrated	3	3171	3132	3209
Sulfur	New	6	305	249	314
	Diluted	3	1630	1342	1842
	Concentrated	3	3992	3982	4002
Chlorine	New	6	28379	25936	30506
	Diluted	3	26682	25649	27266
	Concentrated	3	41460	41332	41594
				Mean ± se	
Carbon	New	6		3491 ± 293	
	Diluted	3		3251 ± 233	
	Concentrated	3		1448 ± 231	
Oxygen	New	6		5903 ± 292	
	Diluted	3		4911 ± 131	
	Concentrated	3		3406 ± 476	
Aluminium	New	6		398 ± 55	
	Diluted	3		366 ± 83	
	Concentrated	3		118 ± 9	

TABLE 6.12

Comparison of the elements (counts per second) detected on the external surface of PVC glove fingers that had been immersed in concentrated or diluted Jetdip® for 24 hours (Dunn's method following One Way ANOVA or Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		Treatments		
		New	Diluted	Concentrated
Carbon	New			
	Diluted	NS		
	Concentrated	<0.05	<0.05	
Oxygen	New			
	Diluted	NS		
	Concentrated	<0.05	<0.05	
Aluminium	New			
	Diluted	NS		
	Concentrated	<0.05	<0.05	
Phosphorus	New			
	Diluted	NS		
	Concentrated	<0.05	NS	
Sulfur	New			
	Diluted	NS		
	Concentrated	<0.05	NS	
Chlorine	New			
	Diluted	NS		
	Concentrated	NS	NS	

6.3.2.1.2 *Polyvinyl chloride glove fingers immersed in Jetdip® for thirty-six hours*
Carbon, oxygen, aluminium and silicon concentrations passed the normality and equal variance tests. There were variations for the concentrations of carbon between treatments ($F_{2,9} = 13.1$, $P = 0.0021$). Oxygen varied between treatments ($F_{2,9} = 10.9$, $P = 0.0040$). There were no differences for aluminium and silicon, but the powers of the executed tests were below the desired power ($F_{2,9} = 1.22$, $P = 0.3405$ and $F_{2,9} = 0.919$ $P = 0.4334$) respectively. Phosphorus differed between treatments ($H = 7.80$, d.f. = 2, $P = 0.0288$). Sulfur varied between treatments ($H = 8.12$, d.f. = 2, $P = 0.0038$). There were differences for chlorine concentrations between treatments ($H = 6.27$, d.f. = 2, $P = 0.0288$). The data are portrayed in Tables 6.13 and 6.14.

TABLE 6.13

Elements as analysed by EDS (counts per second) on PVC glove fingers that had been immersed in concentrated or diluted Jetdip® for 36 hours. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks). The means ± standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Glove treatment	n	Median	25%	75%
Phosphorus	New	6	0	0	0
	Diluted	3	0	0	1
	Concentrated	3	2168	2164	2368
Sulfur	New	6	305	249	314
	Diluted	3	487	460	529
	Concentrated	3	2932	2872	3158
Chlorine	New	6	28379	25936	30506
	Diluted	3	27434	26485	27920
	Concentrated	3	34282	33635	34590
				Mean ± se	
Carbon	New	6		3491 ± 292	
	Diluted	3		4725 ± 440	
	Concentrated	3		2034 ± 27	
Oxygen	New	6		5903 ± 292	
	Diluted	3		6386 ± 532	
	Concentrated	3		3975 ± 19	
Aluminium	New	6		398 ± 55	
	Diluted	3		453 ± 91	
	Concentrated	3		284 ± 66	
Silicon	New	6		507 ± 33	
	Diluted	3		435 ± 51	
	Concentrated	3		486 ± 23	

TABLE 6.14

Comparison of the elements (counts per second) detected on the external surface of PVC glove fingers that had been immersed in concentrated or diluted Jetdip® for 36 hours (Dunn's method following One Way ANOVA or Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		**Treatments**		
		New	Diluted	Concentrated
Carbon	New			
	Diluted	<0.05		
	Concentrated	<0.05	<0.05	
Oxygen	New			
	Diluted	NS		
	Concentrated	<0.05	<0.05	
Phosphorus	New			
	Diluted	NS		
	Concentrated	<0.05	NS	
Sulfur	New			
	Diluted	NS		
	Concentrated	<0.05	NS	
Chlorine	New			
	Diluted	NS		
	Concentrated	NS	NS	

6.3.2.1.3 *Polyvinyl chloride glove fingers immersed in Jetdip® for forty-eight hours*

Phosphorus was the only data set to fail the normality and equal variance tests and there were differences between the treatments (H = 10, d.f. = 2, P = 0.0003). Carbon differed between treatments ($F_{2,9}$ = 20.4, P = 0.0005). There were variations between the treatments for oxygen concentrations ($F_{2,9}$ = 15.1, P = 0.0013). Aluminium did not vary between treatments ($F_{2,9}$ = 0.663, P = 0.5386), but the power of this test was conducted below the optimum power and therefore caution is required for interpretation. Silicon varied between treatments ($F_{2,9}$ = 8.35, P = 0.0089). Sulfur differed very strongly between treatments ($F_{2,9}$ = 383.7, P <0.0001). There were marked differences for chlorine ($F_{2,9}$ = 83.7, P <0.0001). The data are summarised in Tables 6.15 and 6.16.

TABLE 6.15

Elements as analysed by EDS (counts per second) on PVC glove fingers that had been immersed in concentrated or diluted Jetdip® for 48 hours. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks). The means ± standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Glove treatment	n	Median	25%	75%
Phosphorus	New	6	0	0	0
	Diluted	3	123	75	159
	Concentrated	3	1354	1323	1626
				Mean ± se	
Carbon	New	6		3491 ± 293	
	Diluted	3		4879 ± 414	
	Concentrated	3		1600 ± 39	
Oxygen	New	6		5903 ± 292	
	Diluted	3		5704 ± 558	
	Concentrated	3		3262 ± 97	
Aluminium	New	6		398 ± 55	
	Diluted	3		359 ± 93	
	Concentrated	3		289 ± 51	
Silicon	New	6		507 ± 33	
	Diluted	3		422 ± 44	
	Concentrated	3		676 ± 43	
Sulfur	New	6		324 ± 46	
	Diluted	3		500 ± 7	
	Concentrated	3		2327 ± 79	
Chlorine	New	6		28517 ± 1147	
	Diluted	3		24463 ± 1236	
	Concentrated	3		48031 ± 979	

TABLE 6.16

Comparison of the elements (counts per second) of the main elements found on the external surface of PVC glove fingers that had been immersed in concentrated or diluted Jetdip® for 48 hours (Dunn's method following One Way ANOVA or Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements	Treatments			
		New	Diluted	Concentrated
Carbon	New			
	Diluted	<0.05		
	Concentrated	<0.05	<0.05	
Oxygen	New			
	Diluted	NS		
	Concentrated	<0.05	<0.05	
Silicon	New			
	Diluted	NS		
	Concentrated	<0.05	<0.05	
Phosphorus	New			
	Diluted	NS		
	Concentrated	<0.05	NS	
Sulfur	New			
	Diluted	<0.05		
	Concentrated	<0.05	<0.05	
Chlorine	New			
	Diluted	<0.05		
	Concentrated	<0.05	<0.05	

6.3.2.2 Polyvinyl chloride glove fingers immersed in Lorsban®: external surfaces

These results are subdivided into their three different time intervals as in the previous section.

6.3.2.2.1 *Polyvinyl chloride glove fingers immersed in Lorsban® for twenty-four hours*

Carbon and oxygen were the only data sets to pass the normality and equal variance tests. Carbon concentrations differed by treatments ($F_{2,9} = 13.3$, $P = 0.0021$). Oxygen concentrations varied between treatments ($F_{2,9} = 6.94$, $P = 0.0150$). This test was executed below the desired power and caution is needed for the interpretation of this result. There were no variations for aluminium ($H = 1.72$, d.f. = 2, $P = 0.455$) nor for silicon ($H = 0.423$, d.f. = 2, $P = 0.861$). Phosphorus did not differ between

treatments (H = 1.30, d.f. = 2, P = 0.777) nor did sulfur (H = 4.32, d.f. = 2, P = 0.12090. There were no differences for chlorine (H = 3.15, d.f. = 2, P = 0.230). These results are summarised in Tables 6.17 and 6.18.

TABLE 6.17

Elements as analysed by EDS (counts per second) on PVC glove fingers that had been immersed in concentrated or diluted Lorsban® for 24 hours. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks). The means ± standard errors and the difference of the means are shown for the normal distributions (One Way ANOVA).

Elements	Glove treatment	n	Median	25%	75%
Aluminium	New	6	396	272	494
	Diluted	3	482	387	523
	Concentrated	3	691	378	1130
Silicon	New	6	505	428	578
	Diluted	3	482	481	496
	Concentrated	3	523	473	651
Phosphorus	New	6	0	0	0
	Diluted	3	0	0	0
	Concentrated	3	0	0	62
Sulfur	New	6	305	249	314
	Diluted	3	424	417	449
	Concentrated	3	499	459	500
Chlorine	New	6	28379	25936	30506
	Diluted	3	26935	26631	27120
	Concentrated	3	26121	25053	26371
				Mean ± se	
Carbon	New	6		3491 ± 293	
	Diluted	3		7190 ± 333	
	Concentrated	3		5759 ± 1070	
Oxygen	New	6		5903 ± 292	
	Diluted	3		9425 ± 751	
	Concentrated	3		7771 ± 1345	

TABLE 6.18

Comparison of the elements (counts per second) detected on the external surface of PVC glove fingers that had been immersed in concentrated or diluted Lorsban® for 24 hours (Dunn's method following One Way ANOVA or Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		**Treatments**		
		New	Diluted	Concentrated
Carbon	New			
	Diluted	<0.05		
	Concentrated	<0.05	NS	
Oxygen	New			
	Diluted	<0.05		
	Concentrated	NS	NS	

6.3.2.2.2 *Polyvinyl chloride fingers immersed in Lorsban® for thirty-six hours*

Carbon, oxygen and aluminium concentration data passed the normality and equal variance tests. There were strong differences for carbon concentrations between treatments ($F_{3,11} = 39.3$, $P < 0.0001$). Oxygen varied considerably between treatments ($F_{3,11} = 23$, $P < 0.0001$). Aluminium differed between treatments, but the power of the performed test was beneath the optimum power ($F_{3,11} = 5.37$, $P = 0.0160$). There were variations for silicon ($H = 10.2$, d.f. = 3, $P = 0.0167$). Phosphorus varied between treatments ($H = 12.1$, d.f. = 3, $P = 0.0070$) as did sulfur ($H = 11.7$, d.f. = 3, $P = 0.0085$). There were no differences for chlorine ($H = 6.60$, d.f. = 3, $P = 0.0858$). The data are summarised in Tables 6.19 and 6.20.

TABLE 6.19

Elements as analysed by EDS (counts per second) on PVC glove fingers that had been immersed in concentrated or diluted Lorsban® for 36 hours. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks). The means ± standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Glove treatment	n	Median	25%	75%
Silicon	New	6	505	428	578
	Diluted	3	477	376	594
	Concentrated	3	647	625	667
	Taped	3	1794	1670	1911
Phosphorus	New	6	0	0	0
	Diluted	3	0	0	56
	Concentrated	3	2646	2602	2788
	Taped	3	10463	7201	11578
Sulfur	New	6	305	249	314
	Diluted	3	376	341	423
	Concentrated	3	3565	3470	3729
	Taped	3	10661	10301	11982
Chlorine	New	6	28379	25936	30506
	Diluted	3	25836	25071	26057
	Concentrated	3	49609	48644	50052
	Taped	3	45227	19621	101819
				Mean ± se	
Carbon	New	6		3491 ± 293	
	Diluted	3		6501 ± 274	
	Concentrated	3		1265 ± 116	
	Taped	3		4135 ± 371	
Oxygen	New	6		5903 ± 292	
	Diluted	3		7895 ± 480	
	Concentrated	3		2952 ± 271	
	Taped	3		8199 ± 821	
Aluminium	New	6		398 ± 55	
	Diluted	3		384 ± 97	
	Concentrated	3		339 ± 33	
	Taped	3		695 ± 46	

TABLE 6.20

Comparison of the elements (counts per second) detected on the external surface of PVC glove fingers that had been immersed in concentrated or diluted Lorsban® for 36 hours (Dunn's method following One Way ANOVA or Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		Treatments			
		New	Diluted	Concentrated	Taped
Carbon	New				
	Diluted	<0.05			
	Concentrated	<0.05	<0.05		
	Taped	NS	<0.05	<0.05	
Oxygen	New				
	Diluted	<0.05			
	Concentrated	<0.05	<0.05		
	Taped	<0.05	NS	<0.05	
Aluminium	New				
	Diluted	NS			
	Concentrated	NS	NS		
	Taped	<0.05	<0.05	<0.05	
Phosphorus	New				
	Diluted	NS			
	Concentrated	NS	NS		
	Taped	<0.05	NS	NS	
Sulfur	New				
	Diluted	NS			
	Concentrated	NS	NS		
	Taped	<0.05	NS	NS	

6.3.2.2.3 *Polyvinyl chloride fingers immersed in Lorsban® for forty-eight hours*
Only the data for aluminium concentrations passed the equal variance and normality tests, and there were differences between treatments ($F_{3,11} = 4.17$, $P = 0.0336$). This test was performed below the desired power and requires a cautious interpretation. There were no variations for carbon ($H = 7.23$, d.f. = 3, $P = 0.0651$) nor for oxygen ($H = 7.23$, d.f. = 3, $P = 0.0651$). Silicon varied between treatments ($H = 11.2$, d.f. = 3, $P = 0.0106$). Phosphorus differed between treatments ($H = 13.3$, d.f. =3, $P = 0.0040$) as did sulfur ($H = 11.7$, d.f. =3, $P = 0.0085$). There were variations for chlorine ($H = 12.4$, d.f. = 3, $P = 0.0061$). A summary of the data is provided in Tables 6.21 and 6.22.

TABLE 6.21

Elements as analysed by EDS (counts per second) on PVC glove fingers that had been immersed in concentrated or diluted Lorsban® for 48 hours. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks). The means ± standard errors are shown for aluminium (One Way ANOVA).

Elements	Glove treatment	n	Median	25%	75%
Carbon	New	6	3255	2970	4194
	Diluted	3	5257	4354	5310
	Concentrated	3	1600	1550	1651
	Taped	3	5307	2549	6882
Oxygen	New	6	5675	5351	6608
	Diluted	3	5908	4965	6391
	Concentrated	3	3326	3136	3373
	Taped	3	10827	5763	13466
Silicon	New	6	505	428	578
	Diluted	3	422	385	488
	Concentrated	3	712	621	721
	Taped	3	1754	1459	2320
Phosphorus	New	6	0	0	0
	Diluted	3	123	75	159
	Concentrated	3	1354	1323	1626
	Taped	3	9734	6544	10848
Sulfur	New	6	305	249	314
	Diluted	3	495	492	509
	Concentrated	3	2355	2223	2425
	Taped	3	11854	9573	12957
Chlorine	New	6	28379	25936	30506
	Diluted	3	25491	22874	25794
	Concentrated	3	48908	46784	49060
	Taped	3	124118	109044	132339
				Mean ± se	
Aluminium	New	6		398 ± 55	
	Diluted	3		306 ± 119	
	Concentrated	3		289 ± 51	
	Taped	3		761 ± 180	

TABLE 6.22

Comparison of the elements (counts per second) detected on the external surface of PVC glove fingers that had been immersed in concentrated or diluted Lorsban® for 48 hours (Dunn's method following One Way ANOVA or Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		Treatments			
		New	Diluted	Concentrated	Taped
Aluminium	New				
	Diluted	NS			
	Concentrated	NS	NS		
	Taped	<0.05	<0.05	<0.05	
Silicon	New				
	Diluted	NS			
	Concentrated	NS	NS		
	Taped	NS	<0.05	NS	
Phosphorus	New				
	Diluted	NS			
	Concentrated	NS	NS		
	Taped	<0.05	NS	NS	
Sulfur	New				
	Diluted	NS			
	Concentrated	NS	NS		
	Taped	<0.05	NS	NS	
Chlorine	New				
	Diluted	NS			
	Concentrated	NS	NS		
	Taped	NS	<0.05	NS	

6.3.2.3 One minute glove finger immersion: polyvinyl chloride

The results of these two experiments are given separately, the diazinon based insecticide is given first and is followed by the chlorpyrifos based insecticide.

6.3.2.3.1 *Polyvinyl chloride glove fingers immersed in Jetdip®*

All the data sets passed the normality and equal variance tests with the exception of aluminium. Phosphorus was not detected on these samples. Carbon concentrations did not vary between the two treatments ($t = 0.373$, d.f. = 7, $P = 0.7203$). This test was performed below the desired power. Oxygen differed between treatments ($t = -3.78$, d.f. = 7, $P = 0.0069$). Aluminium varied between treatments ($T = 7$, $P = 0.0476$). There were strong differences for silicon ($t = -12.4$, d.f. = 7, $P < 0.0001$). Sulfur differed considerably between treatments ($t = -42.8$, d.f. = 7, $P < 0.0001$).

Chlorine also differed strongly (t = 21, d.f. = 7, P <0.0001). The data are presented in Table 6.23.

TABLE 6.23

Elements (counts per second) detected on PVC glove fingers immersed in Jetdip® for one minute. The means ± standard errors are shown (t test). The medians and percentiles (25th and 75th) are given for aluminium (Mann-Whitney Rank Sum Test)

Elements	Glove finger	n	Mean ± se	Difference of means
Carbon	New	6	5862 ± 1146	637
	Immersed	3	5219 ± 489	
Oxygen	New	6	6027 ± 680	–4365
	Immersed	3	10392 ± 898	
Silicon	New	6	531 ± 64	–2005
	Immersed	3	2536 ± 202	
Sulfur	New	6	390 ± 43	–4776
	Immersed	3	5166 ± 141	
Chlorine	New	6	30437 ± 675	21803
	Immersed	3	8633 ± 487	
			Median **25%** **75%**	
Aluminium	New	6	363 303 494	
	Immersed	3	239 214 286	

6.3.2.3.2 *Polyvinyl chloride glove fingers immersed in Lorsban®*

Oxygen data failed the equal variance test and sulfur failed the normality test. Phosphorus was not detected on these samples. Carbon concentrations did not differ between treatments (t = 0.0689, d.f. = 7, P = 0.9470). There were variations for oxygen concentrations between the two treatments (T = 24, P = 0.0238). Aluminium did not differ between treatments (t = 0.324, d.f. = 7, P = 0.7555). There were strong differences for silicon (t = –8.84, d.f. = 7, P <0.0001). There were differences for sulfur (T = 24, P = 0.0238). There were strong differences for chlorine (t = 13, d.f. = 7, P <0.0001). The data are summarised in Table 6.24. The tests for carbon, aluminium and phosphorus were conducted below the desired power and therefore these results require cautious interpretation.

TABLE 6.24

Elements (counts per second) detected on PVC glove fingers immersed in Lorsban® for one minute. The means ± standard errors and the differences of the means are shown for the normal distributions (Mann-Whitney Rank Sum Test). The medians and percentiles (25th and 75th) are shown for the abnormal distributions (t test).

Elements	Glove finger	n	Mean ± se	Difference of means
Carbon	New	6	5862 ± 1146	136
	Immersed	3	5720 ± 1581	
Aluminium	New	6	479 ± 127	63
	Immersed	3	416 ± 83	
Silicon	New	6	531 ± 64	−1937
	Immersed	3	2468 ± 302	
Chlorine	New	6	30437 ± 675	14253
	Immersed	3	16184 ± 727	
			Median **25%** **75%**	
Oxygen	New	6	6560 4308 6949	
	Immersed	3	11424 9265 16706	
Sulfur	New	6	373 329 475	
	Immersed	3	5675 5513 8858	

6.3.2.4 Polyvinyl chloride gloves immersed in Top Clip Blue Shield®: both surfaces

The results of this group of experiments are subdivided into their three different time intervals.

6.3.2.4.1 *Polyvinyl chloride gloves immersed in Top Clip Blue Shield® for twenty-four hours*

Aluminium, phosphorus and silicon data passed the normality and equal variance tests. The concentration of carbon differed between treatments ($H = 15.2$, d.f. = 2, $P = 0.0005$). There were differences for oxygen between the treatments ($H = 11.4$, d.f. = 2, $P = 0.0034$). Aluminium did not vary between treatments ($F_{2,15} = 2.73$, $P = 0.0977$). This test was conducted below the desired power and therefore this result requires careful interpretation. There were differences between treatments for silicon ($F_{2,15} = 4.81$, $P = 0.0243$). Phosphorus varied greatly between treatments ($F_{2,15} = 137$, $P = <0.0001$). There were differences between treatments for sulfur ($H = 15.2$, d.f. = 2, $P = 0.0005$). Chlorine did not differ between treatments ($H = 2.68$, d.f. = 2, $P = 0.262$). A summary of the data is presented in Tables 6.25 and 6.26.

TABLE 6.25

Elements as analysed by EDS (counts per second) on new, washed and unwashed PVC gloves that had been immersed in Top Clip Blue Shield® for 24 hours. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks). The means ± standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Glove treatment	n	Median	25%	75%
Carbon	New	6	7194	6581	7805
	Washed	6	620	240	843
	Unwashed	6	4605	4550	4751
Oxygen	New	6	6706	5210	7117
	Washed	6	1403	860	1724
	Unwashed	6	6615	6555	6769
Sulfur	New	6	380	337	437
	Washed	6	2351	1492	3316
	Unwashed	6	4737	4601	4806
Chlorine	New	6	31133	30069	35037
	Washed	6	21410	15031	48208
	Unwashed	6	35455	35136	35558
				Mean ± se	
Aluminium	New	6		540 ± 122	
	Washed	6		376 ± 92	
	Unwashed	6		246 ± 19	
Silicon	New	6		574 ± 62	
	Washed	6		456 ± 74	
	Unwashed	6		729 ± 48	
Phosphorus	New	6		0 ± 0	
	Washed	6		1476 ± 280	
	Unwashed	6		4097 ± 125	

TABLE 6.26

Comparison of the elements (counts per second) detected on PVC gloves that had been immersed in Top Clip Blue Shield® for 24 hours (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements	Treatments			
		New	Washed	Unwashed
Carbon	New			
	Washed	<0.05		
	Unwashed	<0.05	<0.05	
Oxygen	New			
	Washed	<0.05		
	Unwashed	NS	<0.05	
Silicon	New			
	Washed	NS		
	Unwashed	NS	<0.05	
Phosphorus	New			
	Washed	<0.05		
	Unwashed	<0.05	<0.05	
Sulfur	New			
	Washed	<0.05		
	Unwashed	<0.05	<0.05	

6.3.2.4.2 *Polyvinyl chloride gloves immersed in Top Clip Blue Shield® for thirty-six hours*

Silicon, sulfur and chlorine data passed the normality and equal variance tests. Carbon differed between treatments (H = 14, d.f. = 2, P = 0.0009). There were differences for oxygen concentrations between the treatments (H = 15.2, d.f. = 2, P = 0.0005). Aluminium varied between treatments (H = 11.4, d.f. = 2, P = 0.0034). There were no variations for silicon concentrations ($F_{2,15}$ = 0.0186, P = 0.9816). Phosphorus differed between treatments (H = 15.7, d.f. = 2, P = 0.0004). There were strong differences for sulfur concentrations between treatments ($F_{2,15}$ = 351.3, P <0.0001). Chlorine also differed significantly between treatments ($F_{2,15}$ = 175, P <0.0001). The data are summarised in Tables 6.27 and 6.28.

TABLE 6.27

Elements as analysed by EDS (counts per second) on new, washed and unwashed PVC gloves that had been immersed in Top Clip Blue Shield® for 36 hours. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks). The means ± standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Glove treatment	n	Median	25%	75%
Carbon	New	6	7194	6581	7805
	Washed	6	1686	1619	1781
	Unwashed	6	360	1303	1433
Oxygen	New	6	6706	5210	7117
	Washed	6	3553	3261	3770
	Unwashed	6	1989	1918	2171
Aluminium	New	6	390	346	681
	Washed	6	185	163	193
	Unwashed	6	176	154	203
Phosphorus	New	6	0	0	0
	Washed	6	366	304	445
	Unwashed	6	1229	1161	1268
				Mean ± se	
Silicon	New	6		574 ± 63	
	Washed	6		601 ± 160	
	Unwashed	6		579 ± 61	
Sulfur	New	6		390 ± 25	
	Washed	6		1866 ± 86	
	Unwashed	6		2350 ± 31	
Chlorine	New	6		33126 ± 1822	
	Washed	6		35918 ± 518	
	Unwashed	6		66958 ± 1568	

TABLE 6.28

Comparison of the elements (counts per second) detected on PVC gloves that had been immersed in Top Clip Blue Shield® for 36 hours (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements	Treatments			
		New	Washed	Unwashed
Carbon	New			
	Washed	<0.05		
	Unwashed	<0.05	<0.05	
Oxygen	New			
	Washed	<0.05		
	Unwashed	<0.05	<0.05	
Aluminium	New			
	Washed	<0.05		
	Unwashed	<0.05	NS	
Phosphorus	New			
	Washed	<0.05		
	Unwashed	<0.05	<0.05	
Sulfur	New			
	Washed	<0.05		
	Unwashed	<0.05	<0.05	
Chlorine	New			
	Washed	NS		
	Unwashed	<0.05	<0.05	

6.3.2.4.3 *Polyvinyl chloride gloves immersed in Top Clip Blue Shield® for forty-eight hours*

Oxygen, silicon and sulfur passed the normality and equal variance tests. Carbon concentrations varied between treatments (H = 13.3, d.f. = 2, P = 0.0013). There were differences for oxygen between treatments ($F_{2,15}$ = 42.5, P <0.0001). Aluminium differed between treatments (H = 12.1, d.f. = 2, P = 0.0023). There were variations for silicon between treatments ($F_{2,15}$ = 4.07, P = 0.0388). This test was executed below the desired power, consequently caution is required for the interpretation of the results. Phosphorus varied between treatments (H = 12.2, d.f. = 2, P = 0.0022) as did sulfur ($F_{2,15}$ = 35.1, P <0.0001). There were no differences for chlorine between the treatments ($F_{2,15}$ = 1.15, P = 0.3434). The results are detailed in Tables 6.29 and 6.30.

TABLE 6.29

Elements as analysed by EDS (counts per second) on new, washed and unwashed PVC gloves that had been immersed in Top Clip Blue Shield® for 48 hours. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks). The means ± standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Glove treatment	n	Median	25%	75%
Carbon	New	6	7194	6581	7805
	Washed	6	992	898	1242
	Unwashed	6	1601	1261	1772
Aluminium	New	6	390	346	681
	Washed	6	209	136	246
	Unwashed	6	143	110	178
Phosphorus	New	6	0	0	0
	Washed	6	842	728	931
	Unwashed	6	794	505	870
				Mean ± se	
Oxygen	New	6		6450 ± 490	
	Washed	6		2167 ± 210	
	Unwashed	6		3294 ±252	
Silicon	New	6		574 ±63	
	Washed	6		414 ± 44	
	Unwashed	6		407 ± 27	
Sulfur	New	6		390 ± 25	
	Washed	6		1425 ± 107	
	Unwashed	6		1783 ± 181	
Chlorine	New	6		33126 ± 1822	
	Washed	6		38463 ± 3516	
	Unwashed	6		38358 ± 2939	

TABLE 6.30

Comparison of the elements (counts per second) detected on PVC gloves that had been immersed in Top Clip Blue Shield® for 48 hours (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

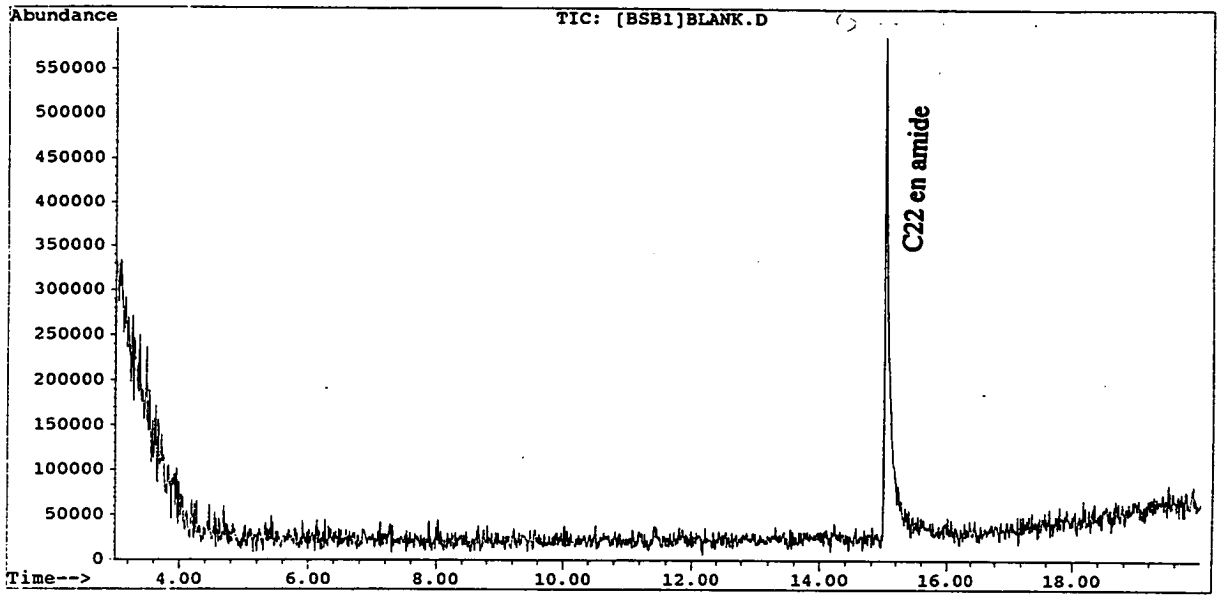
Elements	Treatments			
		New	Washed	Unwashed
Carbon	New			
	Washed	<0.05		
	Unwashed	<0.05	<0.05	
Oxygen	New			
	Washed	<0.05		
	Unwashed	<0.05	<0.05	
Aluminium	New			
	Washed	<0.05		
	Unwashed	<0.05	NS	
Silicon	New			
	Washed	NS		
	Unwashed	NS	NS	
Phosphorus	New			
	Washed	<0.05		
	Unwashed	<0.05	NS	
Sulfur	New			
	Washed	<0.05		
	Unwashed	<0.05	NS	

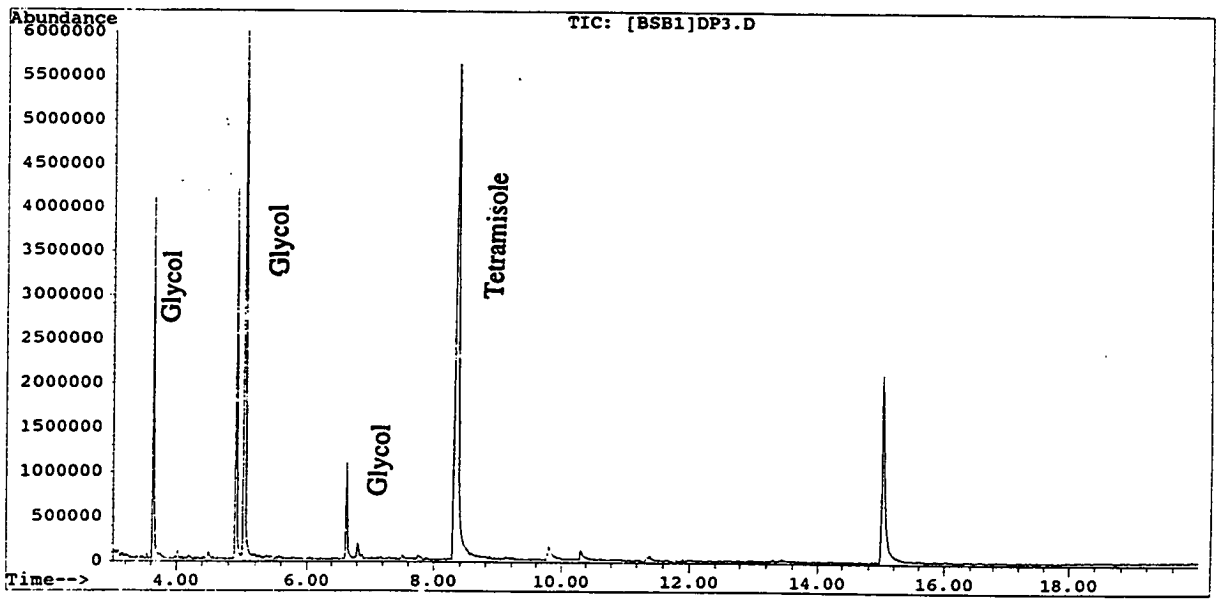
6.3.3 Gas chromatography-mass spectrometry: polyvinyl chloride

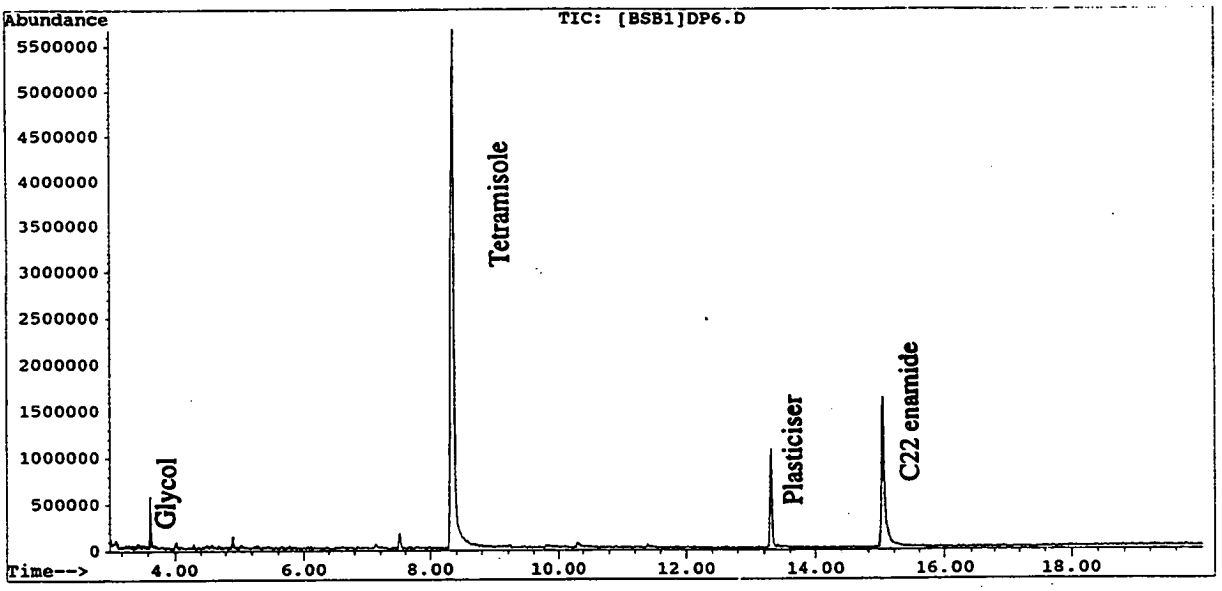
The spectrum from the new glove finger was relatively clear with one peak representing a C22 enamide. The DP 3 glove spectrum had a variety of large glycol peaks and the second highest peak was tetramisole. There were several other peaks that could not be identified. The DP 6 spectrum had a similar profile although there were different unidentified peaks and a plasticiser peak. The OR 1 spectrum had a thermal artefact (an indicator for carbaryl), paclobutrazol and some unidentified peaks that may have been related to pesticides. The OR 13 spectrum was very similar to the control spectrum except for a plasticiser peak. The spectra are illustrated in Figure 6.9.

FIGURE 6.9

GC-MS spectra from the interior of a new PVC glove compared to those from the field



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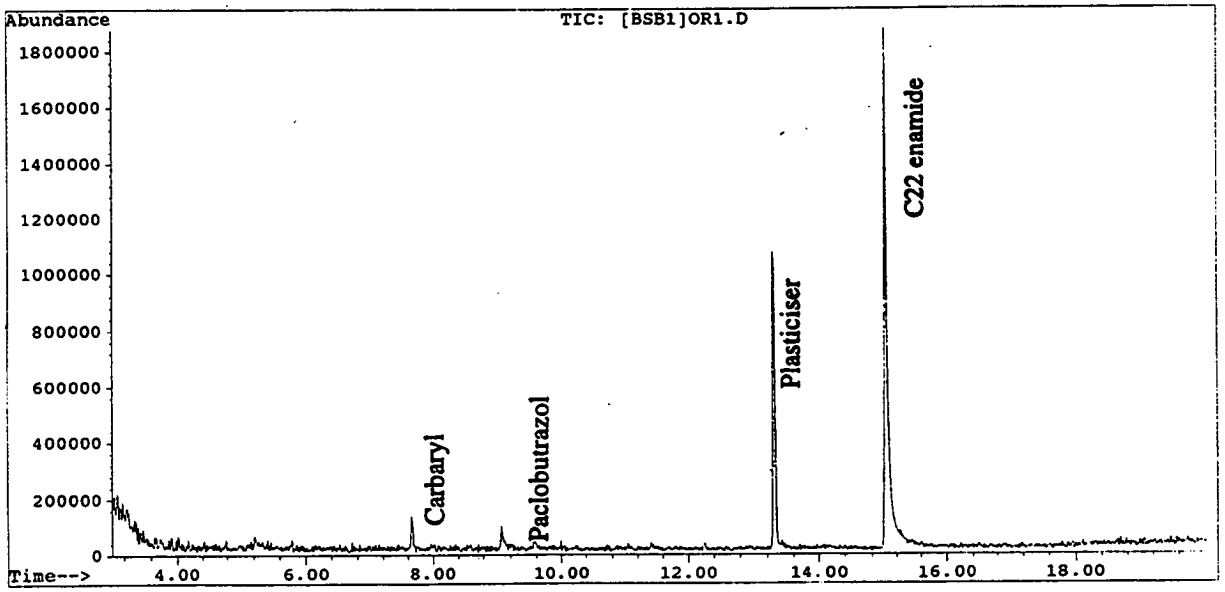
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
Glycol
Tetramisole
Plasticiser
C22 enamide
Time-->
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00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Paclobutrazol
Plasticiser
C22 enamide
Time-->
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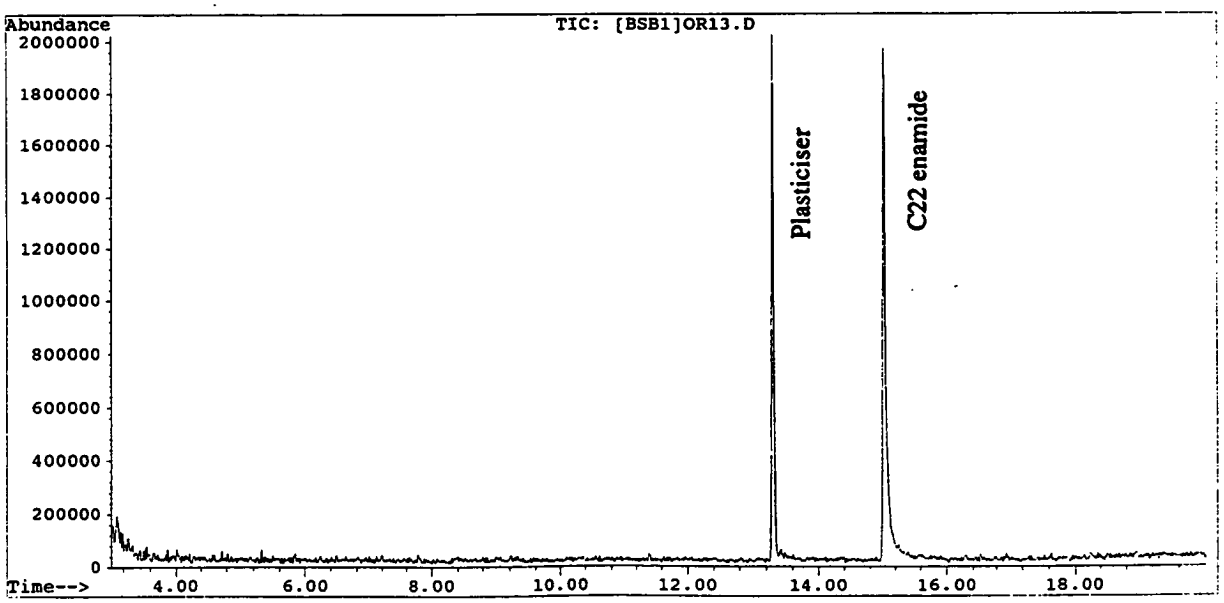
6.00
8.00
10.00
12.00
14.00
16.00
18.00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1200000
1000000
800000
600000
400000
200000
0
Plasticiser
C22 enamide
Time-->
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00

6.3.4 Nitrile-butadiene rubber gloves: immersion experiments

These experiments are presented in the following order: 1) immersions of the external surfaces taken from the non textured palm section, in Jetdip® and Lorsban®; 2) the one minute glove finger immersions in Jetdip® and Lorsban®; and 3) immersion of both sides of NBR in Top Clip Blue Shield®.

6.3.4.1 Immersion of the external surfaces of nitrile-butadiene rubber gloves in Jetdip®

The results of this group of experiments are subdivided into their three different time intervals.

6.3.4.1.1 *Nitrile-butadiene rubber gloves immersed in Jetdip® for twenty-four hours*

Sulfur, carbon and oxygen were the only data sets to pass the equal variance and normality tests. There were strong differences for the concentrations of carbon between treatments ($F_{2,9} = 46.9$, $P < 0.0001$). Oxygen varied convincingly between treatments ($F_{2,9} = 169.5$, $P < 0.0001$). There were no variations for aluminium between treatments ($H = 4.54$, d.f. = 2, $P = 0.103$). Silicon varied between treatments ($H = 9.35$, d.f. = 2, $P = 0.0003$). Phosphorus did not vary between treatments ($H = 3$, d.f. = 2, $P = 0.761$). There were very strong differences for sulfur between the treatments ($F_{2,9} = 253.5$, $P < 0.0001$). Chlorine varied between treatments ($H = 9.35$, d.f. = 2, $P = 0.0003$). Tables 6.31 and 6.32 contain a summary of the data.

TABLE 6.31

Elements as analysed by EDS (counts per second) on NBR gloves that had been immersed (external surface only exposed) in concentrated or diluted Jetdip® for 24 hours. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks). The means ± standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Glove treatment	n	Median	25%	75%
Aluminium	New	6	311	136	965
	Diluted	3	1128	984	2243
	Concentrated	3	1372	1322	1862
Silicon	New	6	674	314	1063
	Diluted	3	2636	2433	2853
	Concentrated	3	4867	3903	5571
Phosphorus	New	6	0	0	0
	Diluted	3	0	0	0
	Concentrated	3	0	0	1049
Chlorine	New	6	18325	6261	29682
	Diluted	3	57361	57339	57919
	Concentrated	3	71198	70097	72237
				Mean ± se	
Carbon	New	6		5228 ± 696	
	Diluted	3		10008 ±326	
	Concentrated	3		17109 ±1418	
Oxygen	New	6		6171 ±791	
	Diluted	3		14995 ±957	
	Concentrated	3		38561 ±2298	
Sulfur	New	6		2680 ±476	
	Diluted	3		8446 ±263	
	Concentrated	3		18513 ±534	

TABLE 6.32

Comparison of the elements (counts per second) detected on the external surface of NBR gloves that had been immersed in concentrated or diluted Jetdip® for 24 hours (Dunn's method following One Way ANOVA or Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements	Treatments			
		New	Diluted	Concentrated
Carbon	New			
	Diluted	<0.05		
	Concentrated	<0.05	<0.05	
Oxygen	New			
	Diluted	<0.05		
	Concentrated	<0.05	<0.05	
Silicon	New			
	Diluted	NS		
	Concentrated	<0.05	NS	
Sulfur	New			
	Diluted	<0.05		
	Concentrated	<0.05	<0.05	
Chlorine	New			
	Diluted	NS		
	Concentrated	<0.05	NS	

6.3.4.1.2 *Nitrile-butadiene rubber gloves immersed in Jetdip® for thirty-six hours*
Carbon, oxygen, silicon and sulfur data passed the normality and equal variance tests, the remainder failed. Carbon concentrations did not vary between treatments ($F_{2,9}$ = 3.11, P = 0.0939). Oxygen varied between treatments ($F_{2,9}$ = 7.11, P = 0.0141). Aluminium did not differ between treatments (H = 0.846, d.f. = 2, P = 0.697) nor did silicon ($F_{2,9}$ = 1.66, P = 0.2435). Phosphorus did not vary between treatments (H = 3, d.f. = 2, P = 0.761). Sulfur differed between treatments ($F_{2,9}$ = 8.67, P = 0.0080). Chlorine did not vary between treatments (H = 1.04, d.f. = 2, P = 0.653). The tests for carbon, oxygen and silicon were performed below the desired power and therefore a cautious interpretation is required. The data are summarised in Tables 6.33 and 6.34.

TABLE 6.33

Elements as analysed by EDS (counts per second) on NBR gloves that had been immersed (external surface only exposed) in concentrated or diluted Jetdip® for 36 hours. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks). The means ± standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Glove treatment	n	Median	25%	75%
Aluminium	New	6	311	136	965
	Diluted	3	241	231	258
	Concentrated	3	287	268	377
Phosphorus	New	6	0	0	0
	Diluted	3	0	0	0
	Concentrated	3	0	0	152
Chlorine	New	6	18325	6261	29682
	Diluted	3	27205	26800	18312
	Concentrated	3	16693	15245	16970
				Mean ± se	
Carbon	New	6		5228 ± 696	
	Diluted	3		2611 ± 848	
	Concentrated	3		4349 ± 405	
Oxygen	New	6		6171 ± 791	
	Diluted	3		8206 ± 621	
	Concentrated	3		10254 ± 335	
Silicon	New	6		700 ± 163	
	Diluted	3		991 ± 214	
	Concentrated	3		1115 ± 24	
Sulfur	New	6		2680 ± 476	
	Diluted	3		3154 ± 182	
	Concentrated	3		5252 ± 100	

TABLE 6.34

Comparison of the elements (counts per second) detected on the external surface of NBR gloves that had been immersed in concentrated or diluted Jetdip® for 36 hours (Dunn's method following One Way ANOVA or Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		Treatments		
		New	Diluted	Concentrated
Oxygen	New			
	Diluted	NS		
	Concentrated	<0.05	NS	
Sulfur	New			
	Diluted	NS		
	Concentrated	<0.05	<0.05	

6.3.4.1.3 *Nitrile-butadiene rubber gloves immersed in Jetdip® for forty-eight hours*

Oxygen and silicon concentrations were the only two data sets to pass the normality and equal variance tests. Carbon concentrations did not differ between treatments ($H = 1.45$, d.f. = 2, $P = 0.536$). There were no variations for oxygen concentrations between treatments ($F_{2,9} = 2.57$, $P = 0.1310$). Aluminium did not differ between treatments ($H = 2.02$, d.f. = 2, $P = 0.390$) nor did silicon ($F_{2,9} = 2.58$, $P = 0.1303$). Tests for oxygen and silicon concentrations were performed below the desired power and caution is required for interpretation of these results. Phosphorus varied between treatments ($H = 10.7$, d.f. = 2, $P = 0.0331$). There were differences for sulfur concentrations between treatments ($H = 6.58$, d.f. = 2, $P = 0.0214$). There were no differences for chlorine ($H = 1.65$, d.f. = 2, $P = 0.476$). The data are presented in Tables 6.35 and 6.36.

TABLE 6.35

Elements as analysed by EDS (counts per second) on NBR gloves that had been immersed (external surface only exposed) in concentrated or diluted Jetdip® for 48 hours. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks). The means ± standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Glove treatment	n	Median	25%	75%
Carbon	New	6	5213	3721	6400
	Diluted	3	4071	3559	4262
	Concentrated	3	4349	4237	4416
Aluminium	New	6	311	136	965
	Diluted	3	376	265	441
	Concentrated	3	652	587	723
Phosphorus	New	6	0	0	0
	Diluted	3	0	0	0
	Concentrated	3	109	69	234
Sulfur	New	6	2409	1617	4017
	Diluted	3	3589	3437	3691
	Concentrated	3	4581	4454	4777
Chlorine	New	6	18325	6261	29682
	Diluted	3	26794	25957	29621
	Concentrated	3	20469	19814	21180
				Mean ± se	
Oxygen	New	6		6171 ± 791	
	Diluted	3		7621 ± 483	
	Concentrated	3		8832 ± 990	
Silicon	New	6		700 ± 163	
	Diluted	3		1160 ± 126	
	Concentrated	3		1170 ± 200	

TABLE 6.36

Comparison of the elements (counts per second) detected on the external surface of NBR gloves that had been immersed in concentrated or diluted Jetdip® for 48 hours (Dunn's method following One Way ANOVA or Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		Treatments		
		New	Diluted	Concentrated
Phosphorus	New			
	Diluted	NS		
	Concentrated	<0.05	<0.05	
Sulfur	New			
	Diluted	NS		
	Concentrated	<0.05	NS	

6.3.4.2 Immersion of the external surfaces of nitrile-butadiene rubber gloves in Lorsban®

These results are subdivided into their three different time intervals.

6.3.4.2.1 *Nitrile-butadiene rubber gloves immersed in Lorsban® for twenty-four hours*

Carbon, aluminium and sulfur were the only data sets to pass the normality and equal variance tests. Carbon concentrations did not differ between treatments ($F_{2,9} = 4.17$, $P = 0.0523$). Oxygen varied between treatments ($H = 8.94$, d.f. = 2, $P = 0.0005$). There were no variations for aluminium ($F_{2,9} = 1.08$, $P = 0.379$). There were differences for silicon between treatments ($H = 9.35$, d.f. = 2, $P = 0.0003$). Phosphorus concentrations varied between treatments ($H = 10.7$, d.f. = 2, $P = 0.0331$). There were very strong differences for sulfur ($F_{2,9} = 101.7$, $P < 0.0001$). Chlorine varied between treatments ($H = 9.35$, d.f. = 2, $P = 0.0003$). The results for carbon and aluminium require cautious interpretation as the tests were conducted below the optimum power. A summary of the data is presented in Tables 6.37 and 6.38.

TABLE 6.37

Elements as analysed by EDS (counts per second) on NBR gloves that had been immersed (external surface only exposed) in concentrated or diluted Lorsban® for 24 hours. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks). The means ± standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Glove treatment	n	Median	25%	75%
Oxygen	New	6	6637	4148	7023
	Diluted	3	13744	13221	14970
	Concentrated	3	18539	15649	22909
Silicon	New	6	674	314	1063
	Diluted	3	2090	2050	2207
	Concentrated	3	3119	2545	3770
Phosphorus	New	6	0	0	0
	Diluted	3	0	0	0
	Concentrated	3	2041	1403	2289
Chlorine	New	6	18325	6261	29682
	Diluted	3	60708	59465	62924
	Concentrated	3	76846	71468	79512
				Mean ± se	
Carbon	New	6		5228 ± 696	
	Diluted	3		7386 ± 375	
	Concentrated	3		8969 ± 1677	
Aluminium	New	6		592 ± 261	
	Diluted	3		508 ± 40	
	Concentrated	3		1081 ± 291	
Sulfur	New	6		2680 ± 476	
	Diluted	3		8057 ± 108	
	Concentrated	3		11573 ± 347	

TABLE 6.38

Comparison of the elements (counts per second) detected on the external surface of NBR gloves that had been immersed in concentrated or diluted Lorsban® for 24 hours (Dunn's method following One Way ANOVA or Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		**Treatments**		
		New	Diluted	Concentrated
Oxygen	New			
	Diluted	NS		
	Concentrated	<0.05	NS	
Silicon	New			
	Diluted	NS		
	Concentrated	<0.05	NS	
Phosphorus	New			
	Diluted	NS		
	Concentrated	<0.05	<0.05	
Sulfur	New			
	Diluted	<0.05		
	Concentrated	<0.05	<0.05	
Chlorine	New			
	Diluted	NS		
	Concentrated	<0.05	NS	

6.3.4.2.2 *Nitrile-butadiene rubber gloves immersed in Lorsban® for thirty-six hours*

Silicon concentrations were the only data to fail the normality and equal variance tests. Phosphorus was not detected on these samples. The concentrations of carbon differed between treatments ($F_{2,9} = 7.86$, $P = 0.0106$). There were marked differences for oxygen concentrations ($F_{2,9} = 32.9$, $P < 0.0001$). Aluminium was tested at slightly below the recommended power and there were variations between treatments ($F_{2,9} = 5.99$, $P = 0.0222$). Silicon varied between treatments ($H = 8.32$, d.f. = 2, $P = 0.0027$). There were strong variations for sulfur ($F_{2,9} = 58.2$, $P < 0.0001$). Chlorine differed between treatments but again this test was conducted below the desired power ($F_{2,9} = 5.17$, $P = 0.0320$). The data are detailed in Tables 6.39 and 6.40.

TABLE 6.39

Elements as analysed by EDS (counts per second) on NBR gloves that had been immersed (external surface only exposed) in concentrated or diluted Lorsban® for 36 hours. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks). The means ± standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Glove treatments	n	Median	25%	75%
Silicon	New	6	674	314	1063
	Diluted	3	3409	2410	4347
	Concentrated	3	3608	2921	3684
				Mean ± se	
Carbon	New	6		5228 ± 696	
	Diluted	3		5818 ± 1256	
	Concentrated	3		10753 ± 1471	
Oxygen	New	6		6171 ± 791	
	Diluted	3		11618 ± 2533	
	Concentrated	3		24885 ± 2537	
Aluminium	New	6		592 ± 261	
	Diluted	3		403 ± 87	
	Concentrated	3		1696 ± 212	
Sulfur	New	6		2680 ± 476	
	Diluted	3		8632 ± 692	
	Concentrated	3		12452 ± 1032	
Chlorine	New	6		18358 ± 5312	
	Diluted	3		55817 ± 4087	
	Concentrated	3		55860 ± 21304	

TABLE 6.40

Comparison of the elements (counts per second) detected on the external surface of NBR gloves that had been immersed in concentrated or diluted Lorsban® for 36 hours (Dunn's method following One Way ANOVA or Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		Treatments		
		New	Diluted	Concentrated
Carbon	New			
	Diluted	NS		
	Concentrated	<0.05	<0.05	
Oxygen	New			
	Diluted	<0.05		
	Concentrated	<0.05	<0.05	
Aluminium	New			
	Diluted	NS		
	Concentrated	<0.05	<0.05	
Silicon	New			
	Diluted	NS		
	Concentrated	<0.05	NS	
Sulfur	New			
	Diluted	<0.05		
	Concentrated	<0.05	<0.05	
Chlorine	New			
	Diluted	NS		
	Concentrated	NS	NS	

6.3.4.2.3 *Nitrile-butadiene rubber gloves immersed in Lorsban® for forty-eight hours*

Chlorine, oxygen, silicon and carbon were the only data groups to pass the normality and equal variance tests. Carbon concentrations did not vary between treatments ($F_{2,9}$ = 1.67, P = 2425) nor did oxygen ($F_{2,9}$ = 1.24, P = 0.3337). There were no variations for aluminium between the treatments (H = 2.54, d.f. = 2, P = 0.318). There were no differences for silicon between treatments ($F_{2,9}$ = 3.56, P = 0.0727). Phosphorus did not vary between treatments (H = 6.55, d.f. = 2, P = 0.264), nor did sulfur (H = 5.15, d.f. = 2, P = 0.0679). Chlorine did not differ between treatments ($F_{2,9}$ = 434, P = 0.6607). The power of the tests for carbon, oxygen, silicon and chlorine was low. The data are summarised in Table 6.41.

TABLE 6.41

Elements as analysed by EDS (counts per second) on NBR gloves that had been immersed (external surface only exposed) in concentrated or diluted Lorsban® for 48 hours. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks). The means ± standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Glove treatment	n	Median	25%	75%
Aluminium	New	6	311	136	965
	Diluted	3	208	134	286
	Concentrated	3	587	421	622
Phosphorus	New	6	0	0	0
	Diluted	3	0	0	0
	Concentrated	3	770	193	874
Sulfur	New	6	2409	1617	4017
	Diluted	3	3897	2852	22653
	Concentrated	3	7248	4912	7361
				Mean ± se	
Carbon	New	6		5228 ± 696	
	Diluted	3		3921 ± 474	
	Concentrated	3		3442 ± 863	
Oxygen	New	6		6171 ± 791	
	Diluted	3		7062 ± 653	
	Concentrated	3		8625 ± 1930	
Silicon	New	6		700 ± 163	
	Diluted	3		1164 ± 233	
	Concentrated	3		1438 ± 254	
Chlorine	New	6		18358 ± 5312	
	Diluted	3		25390 ± 4951	
	Concentrated	3		21584 ± 2879	

6.3.4.3 One minute glove finger immersion: nitrile-butadiene rubber

The results of these two experiments are given separately. The diazinon based insecticide is given first and is followed by the chlorpyrifos based insecticide.

6.3.4.3.1 *Nitrile-butadiene rubber glove fingers immersed in Jetdip®*

All the data passed the normality and equal variance tests. There was no phosphorus detected on these samples. Carbon concentrations did not differ between the treatments ($t = 0.843$, d.f. = 7, $P = 0.4273$). The power of this test was conducted at below the optimum power. There were differences for oxygen ($t = -3.28$, d.f. = 7, $P = 0.0134$). Aluminium did not vary between the treatments and again the power of the test was low. There were marked differences for silicon between the treatments ($t = -806$, d.f. = 3, $P < 0.0001$). Sulfur concentrations varied significantly between treatments ($t = -4.42$, d.f. = 3, $P = 0.0031$). Chlorine did not vary between treatments, but the power of the test was low ($t = 0.741$, d.f. = 7, $P = 0.4830$). The data are summarised in Table 6.42.

TABLE 6.42

Elements (counts per second) detected on NBR gloves immersed in Jetdip® for one minute. The means ± standard errors and the differences of the means are shown (t test).

Elements	Glove finger	n	Mean ± se	Difference of means
Carbon	New	6	6196 ± 761	977
	Immersed	3	5219 ± 489	
Oxygen	New	6	5481 ± 939	–4910
	Immersed	3	10392 ± 894	
Aluminium	New	6	553 ± 269	305
	Immersed	3	249 ± 28	
Silicon	New	6	562 ± 141	–1974
	Immersed	3	2536 ± 202	
Sulfur	New	6	2292 ± 411	–2744
	Immersed	3	5036 ± 232	
Chlorine	New	6	14221 ± 5150	5588
	Immersed	3	86330 ± 487	

6.3.4.3.2 *Nitrile-butadiene rubber glove fingers immersed in Lorsban®*

Oxygen, silicon and sulfur failed the normality and equal variance tests. Phosphorus was not detected on these samples. Carbon concentrations did not differ between the two treatments ($t = 0.313$, d.f. = 7, $P = 0.7635$). Oxygen varied between the two ($T = 23$, $P = 0.0476$). There were no differences for aluminium between treatments ($t = 0.345$, d.f. = 7, $P = 0.7405$). Silicon and sulfur differed between treatments and had the same results ($T = 24$, $P = 0.0238$). There were no differences for chlorine ($t = 0.260$, d.f. = 7, $P = 0.8024$). The tests for carbon, aluminium and chlorine were executed below the desired power. The data are presented in Table 6.43.

TABLE 6.43

Elements (counts per second) detected on NBR gloves immersed in Lorsban® for one minute. The medians and percentiles (25th and 75th) are shown for the abnormally distributed data (Mann-Whitney Rank Sum Test). The means ± standard errors and the differences of the means are shown for the normally distributed data (t test).

Elements	Glove finger	n	Median	25%	75%
Oxygen	New	6	5086	3705	7023
	Immersed	3	11424	9265	16706
Silicon	New	6	374	312	942
	Immersed	3	2250	2129	2861
Sulfur	New	6	1742	1617	3018
	Immersed	3	5675	5513	8858
				Mean ± se	Difference of means
Carbon	New	6		6196 ± 761	476
	Immersed	3		5720 ± 1581	
Aluminium	New	6		553 ± 269	137
	Immersed	3		416 ± 83	
Chlorine	New	6		14221 ± 5150	-1963
	Immersed	3		16184 ± 727	

6.3.4.4 Immersion of both surfaces of nitrile-butadiene rubber gloves in Top Clip Blue Shield®

These results are subdivided into their three different time intervals.

6.3.4.4.1 *Nitrile-butadiene rubber gloves immersed in Top Clip Blue Shield® for twenty-four hours*

Oxygen was the only data set that was normally distributed. Phosphorus was not detected on these samples. Carbon differed between treatments ($H = 9.58$, d.f. = 2, $P = 0.0083$). Oxygen varied between treatments ($F_{2,15} = 6.06$, $P = 0.011$), but the power of the test was low. There were no differences for aluminium ($H = 2.01$, d.f. = 2, $P = 0.3655$). Silicon varied between treatments ($H = 931$, d.f. = 2, $P = 0.0095$) as did sulfur ($H = 1.3$, d.f. = 2, $P = 0.0032$). There were no variations for chlorine ($H = 2.29$, d.f. = 2, $P = 0.318$). The data are given in Tables 6.44 and 6.45.

TABLE 6.44

Elements as analysed by EDS (counts per second) on new, washed and unwashed NBR gloves that had been immersed in Top Clip Blue Shield® for 24 hours. The medians, 25th and 75th percentiles are shown on the abnormally distributed data (Kruskal-Wallis One Way ANOVA on Ranks). The means ± standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Glove treatment	n	Median	25%	75%
Carbon	New	6	5557	3721	7962
	Washed	6	2788	2283	3530
	Unwashed	6	5023	4764	5374
Aluminium	New	6	206	151	394
	Washed	6	383	330	431
	Unwashed	6	386	203	428
Silicon	New	6	656	342	1063
	Washed	6	997	889	1204
	Unwashed	6	1763	1450	2384
Sulfur	New	6	2354	1683	4017
	Washed	6	3003	2927	3348
	Unwashed	6	5007	4830	5395
Chlorine	New	6	18094	6249	29682
	Washed	6	25342	24960	26191
	Unwashed	6	23253	22827	25011
			Mean ± se		
Oxygen	New	6	5592 ± 946		
	Washed	6	6626 ± 1158		
	Unwashed	6	9907 ± 528		

TABLE 6.45

Comparison of the elements (counts per second) detected on NBR gloves that had been immersed in Top Clip Blue Shield® for 24 hours (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks and One Way ANOVA for oxygen). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements	Treatments			
		New	Washed	Unwashed
Carbon	New			
	Washed	<0.05		
	Unwashed	NS	<0.05	
Oxygen	New			
	Washed	NS		
	Unwashed	<0.05	<0.05	
Silicon	New			
	Washed	NS		
	Unwashed	<0.05	<0.05	
Sulfur	New			
	Washed	NS		
	Unwashed	<0.05	<0.05	

6.3.4.4.2 *Nitrile-butadiene rubber gloves immersed in Top Clip Blue Shield® for thirty-six hours*

Carbon concentrations differed between the treatments (H = 7.25, d.f. = 2, P = 0.0233) as did oxygen (H = 9.09, d.f. = 2, P = 0.0106). There were no differences for aluminium between treatments (H = 2.95, d.f. = 2, P = 0.229). Silicon did not vary between treatments (H = 2.85, d.f. = 2, P = 0.2400). Phosphorus was only detected on the unwashed samples and in very small quantities. Consequently, there were no differences between treatments (H = 4.24, d.f. = 2, P = 0.120). Sulfur varied between treatments (H = 9.40, d.f. = 2, P = 0.0091). Chlorine did not differ between treatments (H = 3.79, d.f. = 2, P = 0.1504). The data are presented in Tables 6.46 and 6.47.

TABLE 6.46

Elements as analysed by EDS (counts per second) on new, washed and unwashed NBR gloves that had been immersed in Top Clip Blue Shield® 36 hours. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Elements	Glove Treatment	n	Median	25%	75%
Carbon	New	6	5557	3721	7962
	Washed	6	4974	4809	5127
	Unwashed	6	3702	3663	3711
Oxygen	New	6	5384	3772	7023
	Washed	6	8563	8266	8930
	Unwashed	6	6993	6589	6995
Aluminium	New	6	206	151	394
	Washed	6	338	248	566
	Unwashed	6	216	198	232
Silicon	New	6	656	342	1063
	Washed	6	826	810	1056
	Unwashed	6	1053	980	1103
Phosphorus	New	6	0	0	0
	Washed	6	0	0	0
	Unwashed	6	0	0	34
Sulfur	New	6	2354	1683	4017
	Washed	6	3835	3692	3940
	Unwashed	6	4261	4164	4457
Chlorine	New	6	18094	6249	29682
	Washed	6	23274	22685	24549
	Unwashed	6	18810	17970	19912

TABLE 6.47

Comparison of the elements (counts per second) detected on NBR gloves that had been immersed in Top Clip Blue Shield® for 36 hours (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements	Treatments			
		New	Washed	Unwashed
Carbon	New			
	Washed	NS		
	Unwashed	<0.5	<0.05	
Oxygen	New			
	Washed	<0.5		
	Unwashed	NS	<0.05	
Sulfur	New			
	Washed	NS		
	Unwashed	<0.05	<0.05	

6.3.4.4.3 *Nitrile-butadiene rubber gloves immersed in Top Clip Blue Shield® for forty-eight hours*

There were marked differences for the concentrations of carbon between treatments (H = 15.2, d.f. = 2, P = 0.0005). Oxygen concentrations varied between treatments (H = 11.4, d.f. = 2, P = 0.0033). Aluminium differed between treatments (H = 9.88, d.f. = 2, P = 0.0071) as did silicon (H = 11.4, d.f. = 2, P = 0.0034). Phosphorus was predominantly detected on the unwashed samples and consequently there were differences between the treatments (H = 14.2, d.f. = 2, P = 0.0008). Sulfur varied between treatments (H = 11.4, d.f. = 2, P = 0.0033). There were no differences for chlorine (H = 0.947, d.f. = 2, P = 0.6223). The data are presented in Tables 6.48 and 6.49.

TABLE 6.48

Elements as analysed by EDS (counts per second) on new, washed and unwashed NBR gloves that had been immersed in Top Clip Blue Shield® for 48 hours. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Elements	Glove treatment	n	Median	25%	75%
Carbon	New	6	5557	3721	7962
	Washed	6	1830	1519	2661
	Unwashed	6	1073	1045	1079
Oxygen	New	6	5384	3772	7023
	Washed	6	4518	3635	6266
	Unwashed	6	2341	2302	2376
Aluminium	New	6	206	151	394
	Washed	6	195	164	307
	Unwashed	6	95	76	114
Silicon	New	6	656	342	1063
	Washed	6	638	515	785
	Unwashed	6	214	167	250
Phosphorus	New	6	0	0	0
	Washed	6	0	0	65
	Unwashed	6	271	252	307
Sulfur	New	6	2354	1683	4017
	Washed	6	2495	2200	3029
	Unwashed	6	1233	1166	1356
Chlorine	New	6	18094	6249	29682
	Washed	6	11131	9920	12908
	Unwashed	6	12840	11379	16116

TABLE 6.49

Comparison of the elements (counts per second) detected on NBR gloves that had been immersed in Top Clip Blue Shield® for 48 hours (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements	Treatments			
		New	Washed	Unwashed
Carbon	New			
	Washed	<0.05		
	Unwashed	<0.05	<0.05	
Oxygen	New			
	Washed	NS		
	Unwashed	<0.5	<0.05	
Aluminium	New			
	Washed	NS		
	Unwashed	<0.05	<0.05	
Silicon	New			
	Washed	NS		
	Unwashed	<0.05	<0.05	
Phosphorus	New			
	Washed	NS		
	Unwashed	<0.05	<0.05	
Sulfur	New			
	Washed	NS		
	Unwashed	<0.05	<0.05	

6.3.5 Analyses of defects on used polyvinyl chloride gloves

Cracks in PVC samples were the only defects that could be analysed in a similar manner to the previous EDS work. Analyses of the interior surfaces of some of the cracks in the used PVC gloves and the adjacent areas are summarised in Table 6.50.

TABLE 6.50

Elements detected (counts per second) on the interior surfaces of cracks found in used PVC gloves and adjacent areas.

Glove code	Element	Outside of the crack at 1000 x	Inside of the crack at 1500 x
TF 1	Carbon	1898	3219
	Oxygen	7977	7252
	Aluminium	1188	1113
	Silicon	7583	3946
	Phosphorus	78	24
	Sulfur	608	711
	Chlorine	2474	2552
DP 9		**Outside of the crack at 1000 x**	**Inside of the crack at 2900 x**
	Carbon	4297	2467
	Oxygen	19373	10472
	Aluminium	4150	2789
	Silicon	7723	7331
	Phosphorus	1876	974
	Sulfur	1434	865
	Chlorine	13433	5465
DP 7		**Outside of the crack at 1550 x**	**Inside of the crack at 8000 x**
	Carbon	5863	2996
	Oxygen	9694	7073
	Aluminium	2047	2764
	Silicon	4041	7062
	Phosphorus	292	267
	Sulfur	393	428
	Chlorine	14670	14173

6.3.6 Analyses of contaminants on the used gloves

The PVC glove DP 1 was contaminated with hematite and/or magnetite. This analysis was conducted at 1000 x. A contaminant on DP 3 had the appearance of a fibre and was analysed as carbon at 400 x. DP 7 was contaminated with silicon, carbon, barium, potassium, sulfur, nickel, sodium, magnesium and zinc. BG 5 had a pseudo-hexagonal shaped contaminant on it, which was analysed as talc. In the immersion of PVC in Lorsban® (external surface), there were several long crystals observed on those samples that had been treated with the concentrated solution. These were analysed as gypsum.

6.4 Discussion

The discussion is organised by glove type. Polyvinyl chloride gloves are discussed first followed by NBR, NR, PVC/NBR and finally the thin PVC. The elemental analysis discussion is paired for carbon and oxygen because they are integral to the CPG's composition. Aluminium and silicon are also paired as they form part of the contamination and exposure profile. Phosphorus, sulfur and chlorine are discussed as individual sub-sections.

6.4.1 Polyvinyl chloride gloves

6.4.1.1 Carbon and oxygen

Carbon and oxygen were found in the analyses on the new gloves, as expected. It seems that there is a loss of carbon with use and/or that the carbon is occluded by the contaminants. Oxygen presented a similar profile, although the DP gloves did not differ from the new gloves.

There were differences between the red and the black PVC gloves. New red PVC gloves had the highest concentrations of carbon. The new black PVC gloves appeared to be superior in quality to the red PVC. However, microscopically, the black PVC samples were more difficult than the red PVC to focus on as the black PVC had a substructure (Figure 5.2), which may have been related to an additional protective coating applied by dipping. If this is the case, it may account for the lower carbon concentration as it would have been obscured by the coating. There were significant differences between the new and used gloves from the BG group. This may be related to the usage of the gloves and/or their maintenance history.

The notion of the carbon and oxygen being masked is reinforced by the Jetdip® immersion of the external surfaces and the Top Clip Blue Shield® immersion of both surfaces experiments. In the external surface immersion experiment, carbon and oxygen were detected in the least amounts on the samples that had been immersed in the concentrated Jetdip®. Carbon and oxygen were depleted after the washing technique in the twenty-four hour experiment, but the longer immersion times must have allowed the Top Clip Blue Shield® to adhere more strongly to the surface and did not respond as effectively to the washing technique. Therefore, the Top Clip Blue Shield® covered the surface and consequently carbon and oxygen were not detected in such strong concentrations.

Masking is not evident in the Lorsban® external surfaces experiments. Oxygen and carbon were in higher concentrations on the samples immersed in the diluted

Lorsban® and least on the new samples, in the twenty-four hour interval. The carbon concentrations were similar for the thirty-six hour immersions. The results for oxygen in the thirty-six hour immersion are enigmatic as the taped finger sample had most oxygen but least on the samples immersed in the concentrated formulation. This pattern is repeated for carbon and oxygen in the forty-eight hours immersion. Both the taped finger and the concentrated samples, which were from the same batch, were immersed in neat Lorsban® from the same container, and therefore it was expected that the results should be similar. In both time frames, the neat Lorsban® had permeated through to the interior surfaces of the glove fingers, both taped and un-taped. The unusual results may have been related to the permeation process. The taped glove finger had virtually been sealed off, (therefore separating the interior atmosphere of the glove finger from the external atmosphere), and this would have impeded volatilisation from the interior surface which may have lowered the diffusion gradient, and therefore, permeation was slower. Also, there may have been an interaction of the gloves' exterior surfaces with the cotton knit lining and the Lorsban®.

The one minute immersion experiments did not affect the amount of carbon on the samples. Oxygen was detected in greater quantities on the immersed samples in both experiments. The OP formulations tended to roll off the glove fingers very quickly and it was not expected to have much affect on the carbon concentration. There may have been some interaction between the surface and the OPs and that accounts for the greater quantity of oxygen, but it seems likely that it came from the formulations.

6.4.1.2 Aluminium and silicon

In the exchanged gloves, the highest readings for aluminium and silicon were in the DP group and this may be due to soil contamination. Gibbsite is most common in aluminium rich soil, and this is a characteristic of soil from the Midlands of Tasmania. The higher readings of silicon were from the OR and DP groups, and again this is suggestive of soil residues. The lowest concentrations of aluminium and silicon were from the BG group, doubtless related to their very good condition, having been washed after use.

Aluminium is part of the manufactured black PVC gloves as there were relatively high concentrations in the new gloves. There were no differences between the new and used black PVC and this is most probably related to the fact that they were washed after use and soil residues were removed.

Aluminium only varied at the twenty-four hour time interval in the Jetdip® immersion experiments. Generally there were lower concentrations on the samples immersed in the concentrated formulation and this may be due to a masking effect. There were no significant differences for silicon until the forty-eight hour time interval where there were higher concentrations on the samples immersed in the concentrated Jetdip®. This may have been related to contaminants and/or the products of dissociation of the PVC.

In the Lorsban® immersion experiments; aluminium and silicon concentrations were only significant after the twenty-four hour period. Aluminium concentrations were lowest on the samples immersed in the concentrated formulation and highest on the taped samples. Again this result is rather puzzling given the similarities of the samples. Silicon concentrations were lowest for the diluted samples and highest for the taped samples.

Aluminium concentrations varied in the one minute immersion experiments for Jetdip®, with the higher concentration found on the new glove samples, but not for Lorsban®. Silicon was detected in higher concentrations for the immersed samples. This suggests that silicon was a major component of both the formulations.

Aluminium concentrations became significant after the twenty-four hour time period in the Top Clip Blue Shield® immersion experiments. For all the time periods, there were lower concentrations of aluminium on the unwashed samples and higher concentrations on the new samples, again indicative of a masking effect by the viscous formulation. Silicon concentrations did not follow such a marked trend. There were higher concentrations on the unwashed samples for the twenty-four hour time period and lowest on the washed samples. The remaining time periods were not significant.

6.4.1.3 Phosphorus

No phosphorus was detected on the new red PVC gloves and this suggests that phosphorus had been acquired through the gloves' working conditions, *e.g.* exposure to OPs. The highest concentrations of phosphorus were from the DP group, which were exposed to OP based sheep dips. The higher phosphorus concentrations may also reflect the greater risk of exposure due to the nature of the tasks. Handling sheep through shower jets and dips provides a greater risk of splashing than more mechanised means, *e.g.* using airblast sprayers (Chapter Two, 2.6).

Phosphorus is a constituent only in the new black PVC gloves. The used and new black PVC gloves are again very similar in their amounts of phosphorus, which is probably due to the very good condition of the used black PVC gloves.

In the immersion experiments, the results for Jetdip® and Top Clip Blue Shield® immersions were as anticipated, *i.e.* higher concentrations of phosphorus were found on the samples that had been immersed in the concentrated formulation and in the unwashed samples. In the Lorsban® immersion of the external surfaces experiments, the highest concentrations of phosphorus were detected on the taped finger samples. Again this result was puzzling. Very little phosphorus was detected on the samples from the twenty-four hour immersion. It seems that the phosphorus content of Lorsban® does not adsorb to the surface very well until after twenty-four hours of continuous exposure. It is apparent that, during this time period, permeation becomes noticeable and that taping the finger was a significant factor in increasing the amount of phosphorus on the surface of the glove samples.

In the one minute finger dips, phosphorus was not detected on the samples immersed in Jetdip® and only in insignificant quantities on the samples immersed in Lorsban®.

6.4.1.4 Sulfur

Sulfur was a constituent of both the red and black PVC gloves. All the groups were significantly different from the new samples with the exception of the OR group. It is apparent that sulfur is lost with use. The least amounts of sulfur were on the TF and BG groups, both of which had been washed after use. It therefore seems likely that washing contributes to sulfur loss. In the Top Clip Blue Shield® immersion experiments, the highest quantities of sulfur were found on the unwashed samples as expected. Therefore, it is the usage and number of washes that regulates the rate of loss of sulfur.

Sulfur can be used as an indicator for OP retention only in laboratory conditions. The immersion experiments' results followed a more predictable pattern, with the highest concentrations of sulfur detected on those samples that had been immersed in the concentrated formulations. In the Lorsban® experiments, the taped fingers showed higher concentrations of sulfur than the un-taped fingers.

Sulfur was detected in higher quantities on the immersed gloves for both formulations in the one minute experiments. These were both concentrated formulations and it is highly probable that the sulfur came from the formulations.

6.4.1.5 Chlorine

The results from the exchange program show that the concentrations of chlorine were much higher in the new gloves, suggesting that there is a chlorine loss associated with use and/or masking of the chlorine by contaminants.

In the Jetdip® experiments there were greater concentrations of chlorine found on the samples that had been immersed in the concentrated formulation, and in the one minute experiment there were more on the new samples. It is possible that immersion in concentrated Jetdip®, between one minute and twenty-four hours, initiates migration (Chapter Three, 3.7.2.7) and higher quantities of chlorine were exposed to the detector. In the Lorsban® experiments chlorine concentrations became significant at the forty-eight hours immersion experiment and there were higher concentrations on the taped samples.

6.4.2 Gas chromatography mass spectrometry

The GC-MS results demonstrate that pesticides are retained in the glove matrix, which supports the work of Maddy *et al.* (1985). The new sample's spectrum was fairly clear as anticipated. The water did not dissolve much of the glove matrix and although many of the pesticides found are not highly soluble in water, it did seem to be relatively effective as a solvent for this purpose. The glycol peaks in DP 3 may be associated with pesticides. The tetramisole is a sulphur based sheep/cattle drench (Nilverm®). This was not reported by the respondents in the DP group, but it is common practice for farmers not to regard drenches as farm chemicals; generally farmers refer to them under the generic term of veterinary chemicals. The thermal artefact in OR 1 is associated with carbaryl, which decomposes in the GC column. Paclobutrazol is a growth inhibitor found in products such as Cultar® and Clipper®.

6.4.3 Nitrile-butadiene rubber gloves

The NBR glove samples from the exchange program are discussed first. All the experimental work was with Sol-Vex™ gloves and both sections are discussed under the various elemental headings.

6.4.3.1 Carbon and oxygen

The results for carbon and oxygen for Sol-Vex™ and MSA™ gloves were dissimilar. Carbon and oxygen were detected in higher quantities in the used Sol-Vex™ and the new MSA™ gloves. This merely highlights the different composition of the gloves, because both of these types of gloves had been treated in a similar manner and all the used ones had been washed in detergent and water.

The results from the immersion experiments were similar. In the Jetdip® experiments, the higher concentrations of carbon and oxygen were detected on those samples that had been immersed in the concentrated formulation for twenty-four hours. After twenty-four hours the differences in carbon concentrations became insignificant. This was the same for oxygen after thirty-six hours. The lowest concentrations were found on the new samples. The Lorsban® immersion experiments had higher concentrations of carbon and oxygen on the samples immersed in the concentrated formulation until the forty-eight hour period, after which there were no significant differences. In the one minute experiments carbon was not significantly different and oxygen was detected in higher concentrations on the immersed samples.

Apparently carbon and oxygen are components of the formulations. It is only after a certain time, when the permeation process is under way, that carbon and oxygen are retained on the surface and later lost either by diffusion or volatilisation.

6.4.3.2 Aluminium and silicon

Aluminium and silicon were components of the new Sol-Vex™ and the new MSA™ gloves. The concentrations of these elements were diminished with use.

Jetdip® immersions did not influence the concentrations of aluminium or silicon, except after twenty-four hours immersion when there was a higher concentration of silicon on the samples immersed in the concentrated formulation. Aluminium concentrations did not vary in the Lorsban® experiments, except for the thirty-six hours immersion when there were higher concentrations on the samples that had been immersed in the concentrated formulation and less on those immersed in the diluted formulation. In the Top Clip Blue Shield® experiments, aluminium concentrations decreased on the unwashed samples, with higher concentrations found on the new samples. Top Clip Blue Shield® adhered to the surface of the samples after forty-eight hours and shielded the aluminium concentrations from the detector.

Silicon was detected in greater quantities on the samples immersed in the concentrated Lorsban® experiments at twenty-four and thirty-six hours, but not at forty-eight hours. At this later time the Lorsban® may have permeated to the NBR and conceivably masked the silicon, which is intrinsic to the glove.

In the one minute immersion experiments, silicon is significant in both experiments and had the higher concentrations on the immersed samples. This is a similar finding to the PVC samples and this indicates that silicon is a constituent of these OPs.

6.4.3.3 Phosphorus

Phosphorus was not detected on any of the new gloves and therefore all the phosphorus came from OP exposure. Very small quantities were found on both types of used gloves and hence most of the phosphorus was removed by the washing and/or drying techniques used on this farm.
In the sheep dip experiments, phosphorus was detected after the twenty-four hours immersion in Top Clip Blue Shield® on the unwashed samples and on the samples that had been immersed for forty-eight hours in the concentrated Jetdip®. These times were required by the concentrated sheep dips to permeate to the gloves and to reside in and on the surface until phosphorus was retained in significant quantities.

In the Lorsban® experiments, it was detected in significant quantities on the samples immersed in the concentrated formulation at twenty-four hours. This result is somewhat puzzling as there was no phosphorus detected at thirty-six hours, and, at forty-eight hours, it was only detected on the samples immersed in the concentrated formulation (but these findings were not significant). Perhaps the phosphorus was masked by a by-product from the permeation process.

One minute immersion was not long enough for phosphorus to adhere to the glove surface or perhaps it was lost through volatilisation.

6.4.3.4 Sulfur

Sulfur is a component of MSA™ and Sol-Vex™ gloves (Chapter Three, 3.6.2). There was much less sulfur on the used gloves than the new, and therefore sulfur was lost with use or from the washing techniques.

In all the immersion experiments, there is a general trend for sulfur to be retained on the surface of those samples that were immersed in the concentrated formulations, but there were some interesting exceptions. In the Jetdip® immersion experiments, there were no variations in the results, sulfur being detected in much higher concentrations in all of the samples immersed in the concentrated formulations and lower in the new samples. Therefore, sulfur can be used as an indicator for Sol-Vex™ gloves exposed to Jetdip®. In the Top Clip Blue Shield® experiments, this trend was replicated, the unwashed samples having the highest concentrations of sulfur, except for the forty-eight hour immersion period after which the sulfur concentrations became insignificant. This pattern was repeated in the Lorsban® experiment, as the concentrations were higher in the concentrated formulation until the forty-eight hour immersion period after which they became insignificant. It is possible that the

permeation process had progressed further and that most of the sulfur had either diffused through the surface or was masked by other products.

Sulfur was detected in higher concentrations on the immersed samples in the one minute immersion experiments. Thus, sulfur can only be an indicator for OP contamination until thirty-six hours continuous exposure for diazinon and chlorpyrifos based products.

6.4.3.5 Chlorine

Chlorine is a component of both types of NBR gloves and the concentrations decrease with use. Generally chlorine was not significant in all the immersion experiments. It was a significant finding in the Jetdip® experiments at twenty-four hours and the Lorsban® experiments at twenty-four and thirty-six hours, where more was detected on the samples that had been immersed in the concentrated formulations. Generally, the formulations are able to occlude the chlorine from the detector.

6.4.4 Natural rubber gloves

Hy-Care™ gloves are discussed first followed by the washing-up gloves.

6.4.4.1 Hy-Care™ gloves

Carbon was a component of the new Hy-Care gloves and was not significantly different between new and used gloves. Oxygen and silicon concentrations were much higher in the OR group and this may be related to contamination. Phosphorus concentrations were higher in the OR group, which may be an indicator for OP retention. There was very little phosphorus detected on the TF gloves. Again this is probably related to their washing procedures. Sulfur was detected in slightly higher concentrations on the new gloves and therefore cannot be used as a sole indicator for OP exposure. There was very little chlorine detected on these gloves. However, the concentrations were higher in the OR group. Perhaps these gloves had been used more extensively, and, if there is a protective outer coating it may have been eroded with use and the chlorine exposed.

6.4.4.2 Washing-up gloves

Oxygen, silicon and phosphorus differed between the new and the used washing-up gloves. The first two elements were detected in greater concentrations on the new gloves, and hence they are integral components of the material. Phosphorus was detected in higher concentrations on the used gloves and this indicates some form of contamination, possibly a fertiliser, as no OPs were used with these gloves. Chlorine concentrations decreased with use.

6.4.5 Polyvinyl chloride/nitrile-butadiene rubber gloves

The grubbiness of the used PVC/NBR gloves is most likely to be related to soil residues because of the high readings of silicon and aluminium. Carbon, chlorine and sulfur are components of the new gloves and their concentrations decreased with use, or the soil residues may have masked their presence. These gloves had been stored on the tractor cab floor, were five years old and had never been washed. Consequently the soil residue contamination was not unexpected.

6.4.6 Thin polyvinyl chloride gloves

It is difficult to interpret these results given the inability to compare them to new gloves. The relatively large chlorine peak suggests that they are a type of PVC. The high concentrations of silicon and aluminium indicate that the gloves were contaminated with soil. Phosphorus was not detected in very high concentrations. Sulfur was much higher, although it is impossible to predict whether this was due to contamination or is part of the material.

6.4.7 Defect analyses

This type of analysis was more difficult because of the higher magnification necessary. It was not possible to maintain the same magnification for the interior of the cracks and the area outside the crack, because other defects and or contaminants encroached into the field of view. Therefore, the viewing was conducted at differing magnifications, and consequently it is not possible to compare elemental concentrations inside and outside the cracks. Thus, this was not an effective method to determine if OPs resided in greater concentrations in the defects.

6.4.7 Contaminants

The mineral contamination on the DP 1 glove demonstrates that this glove was contaminated by an iron rich soil common to the Midlands of Tasmania, from where the glove came. The contaminants on DP 7 were representative of fly ash. The gypsum detected on the PVC samples immersed in the concentrated Lorsban® is probably from a building product and indicates some cross contamination. The fume hood in which the experiments were conducted was not made from products containing gypsum. It is not known where the contamination occurred.

6.5 Chapter Summary And Conclusions

Energy-dispersive-spectroscopy has been established as an effective method in ascertaining the main elements used in the manufacture of CPGs or to which the gloves have been exposed. This information about the inherent elements has not been

readily available to the public because of issues surrounding confidentially. New CPGs have been compared to used gloves.

The GC-MS method and the EDS method were complementary. It was established that pesticides can be detected from the glove linings on used gloves using GC-MS. Phosphorus and sulfur have been used as indicators to ascertain exposure to OPs with varying success. Phosphorus can act an indicator for red PVC gloves exposed to sheep dips for over twenty-four hours continuous exposure and following field use. Sulfur is lost with use and can only act as an indicator for OP exposure in controlled laboratory conditions. Phosphorus can cautiously be used as an indicator for OP exposure on NBR gloves. Sulfur in an ineffective indicator for OP exposure on NBR gloves from field use and has limited use in controlled laboratory experiments.

The concentrations of the elements of interest can be distorted by occlusion, through external coatings or by contaminants.

The EDS method could be used in conjunction with other established methods of permeation testing (Chapter Three, 3.7). There were some discrepancies in the immersion experiments, particularly at the thirty-six hour time period. It seems that this period is a dynamic time for permeation processes.

There were some inconsistencies for the aluminium concentrations. While aluminium is an indicator for soil contamination, it cannot be ignored that the punch was aluminium, and, although it was sharpened several times, there may have been some contamination on the samples that were transferred from the punch. The stubs were also made of aluminium and again this may have been a source of contamination as the taped samples were punched out at a later time than the concentrated samples, there is a possibility that the punch was more worn then and perhaps some contamination came from the punch.

This chapter has identified the chemical composition of selected CPGs. Used CPGs have had a chemical profile completed and compared to new gloves thus providing important information about their chemical characteristics. Ultraviolet radiation is an important contributing agent to polymer degradation and this is investigated in the next chapter.

Chapter Seven

The Effects Of Organophosphorus Compounds (Insecticides) And Weathering Upon Chemically Protective Gloves

7.1 Introduction

The effect of UV irradiation and weathering upon polymers and elastomers has been previously discussed in Chapters Three (3.3.2.2.1 and 3.4.1) and Five (5.1). This chapter examines the short-term and long-term effects of sunlight exposure in combination with OP exposures upon CPGs.

The aims of these experiments were:

1. to determine the short-term effects of sunlight, Top Clip Blue Shield®, Lorsban® and Malathion® on PVC and NBR gloves on typical days when spraying/dipping could have been conducted;
2. to monitor the progress of physical and chemical degradation during long-term exposure to sunlight; and
3. to compare controlled embrittlement to that caused by long-term exposure.

7.2 Materials And Methods

All the gloves used in these studies were purchased from East-Side Agencies Pty Ltd., Hobart, and were all from the same batches. Red PVC and Sol-Vex™ gloves were used in these experiments.

The same two phosphorothionates Top Clip Blue Shield® and Lorsban® were used as detailed in Chapter Five (5.2.2.1). Additionally a phosphorothionothiolate, Malathion®, was used (CAS 121–75–5, Chemspray Pty. Ltd. Australia, a.i. maldison 500 g/L with 487 g/L hydrocarbon solvent. Date of manufacture July 1993 batch 825, from Roberts Pty. Ltd., Huonville, Tasmania). Malathion and maldison are synonyms for the a.i. of Malathion®. For the long-term exposure experiment only Top Clip Blue Shield® was used.

7.2.1 Short-term exposure experiments

Fifty-six specimens measuring 5 cm x 5 cm were cut from the dorsal surfaces of randomly selected PVC gloves and the same number from Sol-Vex™ gloves. The glove specimens were then placed in cardboard containers with the exterior surface upward.

New hypodermic glass syringes fitted with 17 gauge needles were used to spray the exterior surfaces of five PVC and five Sol-Vex™ specimens using 0.5 mL of dilute insecticides. All insecticides were diluted with water to meet application recommendations on their container labels. Top Clip Blue Shield® was diluted to give diazinon 0.1 gm/L, for dipping. Lorsban® was diluted to give chlorpyrifos 0.25 g/L for wingless grasshoppers. Malathion® was diluted to give maldison 5 g/L for

aphids. The same method was repeated with concentrated insecticides straight from the container. Once the glove specimen had been treated, a soft paint brush was gently applied to the glove sample surface to evenly spread the insecticide.

Each experiment had four control specimens. Two of these were covered with a lid that allowed air movement over the specimen but occluded direct sunlight and the other two were exposed to sunlight.

These specimens in their respective containers were exposed to sunlight on the roof of the Geography Department at the University of Tasmania for four hours from 1100–1500 hours. Ambient temperatures were recorded using a Min-Max thermometer (Brannan-England) and the mean for the exposure period was determined. Ultraviolet radiation was measured and recorded (UV-Biometer, Solar Light Co. Ltd, Model 501) every ten minutes. The UV Biometer was connected to a Campbell Scientific Micrologger, which in turn was connected to a Sun Sparc station to capture the data. The results were converted from milliwatts (mW) to kilojoules (kJ).

After this four hour exposure period the glove specimens were rinsed with distilled water to remove any airborne contaminants and air dried in a fume hood. The specimens were then sampled and mounted as described in Chapter Five (5.2.1). They were stored in specially prepared boxes and kept at 4°C until analysed by the ESEM as described in Chapter Five (5.2.3).

Variables measured included: grid coordinates; glove type; replicate number; chemical concentration; temperature, UV radiation and date of experiment. Defect variables were the same as in Chapter Five.

X-ray microanalysis facilities were unavailable at the time of these experiments. The samples could not be kept as this would have increased the pesticide exposure time.

7.2.2 Long-term exposure experiments

New intact gloves were coded and labelled inside their cuffs with indelible ink. Additionally, labels were wrapped in plastic and placed inside the body of the gloves. The gloves were placed on a wooden railing with their dorsal surfaces uppermost. They were tied on with electric fencing wire over the fingers and over the cuffs. Five Sol-Vex™ and five PVC gloves were treated with concentrated Top Clip Blue Shield® and another five each treated with diluted Top Clip Blue Shield®. The insecticide was diluted and applied in the same manner as in the short-term sunlight exposure study. Two gloves of each type were untreated. The same UV Biometer was used. These

experiments began in March 1995 and were terminated seven months later. On the first day of every month a specimen was cut from the dorsal surface of the gloves, with an approximate size of 2 cm x 2 cm. The specimens were placed in individual brown paper bags that were labelled with the appropriate glove code and date. These specimens were stored in a cabinet until samples could be prepared for ESEM analysis, in the same manner as described above. Samples were also prepared from the dorsal surfaces of new gloves from the same batches. The gloves were inspected for visible degradation. These samples were also analysed with the EDS method described in Chapter Six (6.2).

7.2.3 Liquid nitrogen immersion experiments

An exploratory experiment was conducted to determine if there were any differences between freeze fractured specimens and those from the long-term exposures. Specimens were cut from new PVC and Sol-Vex™ gloves in a haphazard manner. In total four specimens were tested. Each specimen was immersed in a small container filled with liquid nitrogen and left there until frozen stiff, removed with forceps and then smashed with a cotton-gloved fist. This procedure was conducted on one PVC and one NBR specimen. The remaining two specimens were immersed in the container of liquid nitrogen and when they were frozen stiff they were still held in the liquid nitrogen with two snub nosed pliers attached to each side and fractured by snapping the specimen. The samples were mounted in the manner previously described and examined in the ESEM with the same operating conditions discussed in Chapter Five (5.2.3).

7.2.4 Statistical analyses

The data for the short-term exposure studies were not normally distributed (Kolmogorov-Smirnov Test) nor were variances equal (Levene Median Test) and therefore Kruskal-Wallis One Way ANOVA on Ranks using the statistical program SigmaStat™ was used. The medians, 25th and 75th percentiles have been rounded to the nearest whole number. The results of all pairwise multiple comparison tests were ascertained with Dunn's Test since the sample sizes were unequal. The data for the long-term exposure study were statistically variable. The abnormal distributions were treated as for the short-term exposure studies. The normal distributions were analysed with a One Way ANOVA. The means and standard errors have been recorded and were rounded to the nearest whole number. This was followed with an all pairwise multiple comparison procedure using Student-Newman-Keuls method or Dunn's method where applicable.

7.3 Results

7.3.1 Short-term exposures: polyvinyl chloride

While each experiment had four groups with the same sample sizes they were not the same on the completion of the experiment, as some were lost due to atmospheric conditions.

The results are discussed according to dates. There were no slumps on the PVC gloves as in Chapter Five (5.3). Table 7.1 details the dates of the experiments and insecticides used.

TABLE 7.1

Description of the experimental conditions to assess short-term exposures to natural UV-B and three organophosphorus compounds (insecticides)

Date	Glove	Insecticides	Time	Mean temperature	UV-B kJ/m^2
6/4/95	PVC	Diazinon	1100–1500	18°	0.456
6/4/95	Sol-Vex™	Diazinon	1100–1500	18°	0.456
28/4/95	PVC	Diazinon	1100–1500	24.5°	0.677
28/4/95	Sol-Vex™	Diazinon	1100–1500	24.5°	0.677
10/5/95	PVC	Chlorpyrifos	1100–1500	19°	0.051
10/5/95	Sol-Vex™	Chlorpyrifos	1100–1500	19°	0.051
10/5/95	PVC	Diazinon	1100–1500	19°	0.051
10/5/95	Sol-Vex™	Diazinon	1100–1500	19°	0.051
10/5/95	PVC	Malathion	1100–1500	19°	0.051
10/5/95	Sol-Vex™	Malathion	1100–1500	19°	0.051

7.3.1.1 Polyvinyl chloride gloves exposed to weathering on the 6/4/95 and Top Clip Blue Shield®

There were no differences for cracks between treatments ($H = 3.63$, d.f. = 3, $P = 0.305$. There were differences for cavities between treatments ($H = 19$, d.f. = 3, $P = 0.0003$). Convexities varied by treatments ($H = 10.1$, d.f. = 3, $P = 0.0179$). There were very few smooth areas and they did not differ by treatment ($H = 1.80$, d.f. = 3, $P = 0.615$. Contaminants differed between treatments ($H = 12$, d.f. = 3, $P = 0.0074$). A summary of the data is provided in Tables 7.2 and 7.3.

TABLE 7.2

Defects per unit area on the surface of PVC gloves following exposure to the outdoor environment and Top Clip Blue Shield® on the 6/4/95. The samples were covered, exposed, treated with concentrated insecticide or diluted insecticide. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatment	n	Median	25%	75%
Cavities	Covered	20	3	2	4
	Exposed	20	4	4	5
	Concentrated	50	5	2	10
	Diluted	50	5	4	6
Contaminants	Covered	20	0	0	1
	Exposed	20	0	0	1
	Concentrated	50	1	0	4
	Diluted	50	0	0	1
Convexities	Covered	20	2	1	3
	Exposed	20	4	3	5
	Concentrated	50	4	1	11
	Diluted	50	5	2	7
Cracks*	Covered	20	0	0	0
	Exposed	20	0	0	0
	Concentrated	50	0	0	0
	Diluted	50	0	0	0
Smooth†	Covered	20	0	0	0
	Exposed	20	0	0	0
	Concentrated	50	0	0	0
	Diluted	50	0	0	0

* The mean for cracks = 0.014
† The mean for smooth = 0.007

TABLE 7.3

Comparison of the defects per unit area on the surface of PVC gloves following exposure to a diazinon based insecticide on the 6/4/95. The samples were covered, exposed, treated with concentrated insecticide and diluted insecticide. (Dunn's method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		**Treatment**			
		Covered	Exposed	Concentrated	Diluted
Cavities	Covered				
	Exposed	NS			
	Concentrated	<0.05	NS		
	Diluted	<0.05	NS	NS	
Contaminants	Covered				
	Exposed	NS			
	Concentrated	<0.05	NS		
	Diluted	NS	NS	NS	
Convexities	Covered				
	Exposed	NS			
	Concentrated	<0.05	NS		
	Diluted	<0.05	NS	NS	

7.3.1.2 Polyvinyl chloride gloves exposed to weathering on the 28/4/95 and Top Clip Blue Shield®

There were no differences between treatments for cracks (H = 2.54, d.f. = 3, P = 0.4683). Cavities did not differ between treatments (H = 6.21, d.f. = 3, P = 0.1017). Convexities differed between treatments (H = 13.1, d.f. = 3, P = 0.0045). Contaminants differed strongly (H = 33.1, d.f. = 3, P <0.0001). These samples did not exhibit any smooth areas. The data are summarised in Tables 7.4 and 7.5.

TABLE 7.4

Defects per unit area on the surface of PVC gloves following exposure to the outdoor environment and Top Clip Blue Shield® on the 28/4/95. The samples were covered, exposed, treated with concentrated insecticide and diluted insecticide. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatment	n	Median	25%	75%
Cavities	Covered	20	4	4	4
	Exposed	10	4	3	4
	Concentrated	50	4	3	5
	Diluted	50	3	3	4
Contaminants	Covered	20	4	4	6
	Exposed	10	5	4	7
	Concentrated	50	2	0	4
	Diluted	50	2	1	3
Convexities	Covered	20	4	3	5
	Exposed	10	4	2	4
	Concentrated	50	3	2	5
	Diluted	50	2	2	3
Cracks*	Covered	20	0	0	0
	Exposed	10	0	0	0
	Concentrated	50	0	0	0
	Diluted	50	0	0	0

* The mean for cracks = 1.75

TABLE 7.5

Comparison of the defects per unit area on the surface of PVC gloves following exposure to a diazinon based insecticide on the 28/4/95. The samples were covered, exposed, treated with concentrated insecticide or diluted insecticide. (Dunn's method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		Treatment			
		Covered	Exposed	Concentrated	Diluted
Contaminants	Covered				
	Exposed	NS			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	NS	
Convexities	Covered				
	Exposed	NS			
	Concentrated	NS	NS		
	Diluted	<0.05	NS	NS	

7.3.1.3 Polyvinyl chloride gloves exposed to weathering on the 10/5/95 and Lorsban®

There were no differences for cracks within the treatments (H = 2.33, d.f. = 3, P = 0.5067). Cavities did not differ between treatments (H = 4.83, d.f. = 3, P = 0.185). There were no variations for convexities (H = 2.28, d.f. 3, P = 0.516). Contaminants differed between treatments (H = 18.4, d.f. = 3, P = 0.0004). There were no smooth areas on these samples. A summary of the data is presented in Tables 7.6 and 7.7.

TABLE 7.6

Defects per unit area on the surface of PVC gloves following exposure to the outdoor environment and Lorsban® on the 10/5/95. The samples were covered, exposed, treated with concentrated insecticide or diluted insecticide. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatment	n	Median	25%	75%
Cavities	Covered	20	4	4	5
	Exposed	20	4	4	4
	Concentrated	50	5	4	5
	Diluted	50	5	4	5
Contaminants	Covered	20	2	0	3
	Exposed	20	3	2	4
	Concentrated	50	4	2	6
	Diluted	50	3	2	4
Convexities	Covered	20	4	2	5
	Exposed	20	4	3	5
	Concentrated	50	4	3	5
	Diluted	50	4	3	5
Cracks*	Covered	20	0	0	0
	Exposed	20	0	0	0
	Concentrated	50	0	0	0
	Diluted	50	0	0	0

* The mean for cracks = 0.057.

TABLE 7.7

Comparison of the defects per unit area on the surface of PVC gloves following exposure to a chlorpyrifos based insecticide on the 10/5/95. The samples were covered, exposed, treated with concentrated insecticide or diluted insecticide. (Dunn's method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defect		**Treatment**			
		Covered	Exposed	Concentrated	Diluted
Contaminants	Covered				
	Exposed	NS			
	Concentrated	<0.05	NS		
	Diluted	NS	NS	<0.05	

7.3.1.4 Polyvinyl Chloride Gloves exposed to weathering on the 10/5/95 and Malathion

Cracks did not differ between the treatments (H = 2, d.f. = 3, P = 0.5724. Cavities differed strongly between treatments (H = 25.9, d.f. = 3, P = <0.0001). Convexities also varied between groups, but not as strongly (H = 18.5, d.f. = 3, P = 0.0003). There were no slumps on these samples and few smooth areas, which were not significantly different between groups (H = 2, d.f. = 3, P = 0.572). Contaminants varied between treatments (H = 18.7, d.f. = 3, P = 0.0003). The data are summarised in Tables 7.8 and 7.9.

TABLE 7.8

Defects per unit area on the surface of PVC gloves following exposure to the outdoor environment and Malathion® on the 10/5/95. The samples were covered, exposed, treated with concentrated insecticide or diluted insecticide. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatment	n	Median	25%	75%
Cavities	Covered	20	4	4	5
	Exposed	20	4	4	4
	Concentrated	40	4	3	6
	Diluted	40	6	5	7
Contaminants	Covered	20	2	0	3
	Exposed	20	3	2	4
	Concentrated	50	2	1	4
	Diluted	50	4	2	7
Convexities	Covered	20	4	2	5
	Exposed	20	4	3	5
	Concentrated	50	3	0	5
	Diluted	50	5	4	6
Cracks*	Covered	20	0	0	0
	Exposed	20	0	0	0
	Concentrated	40	0	0	0
	Diluted	40	0	0	0
Smooth†	Covered	20	0	0	0
	Exposed	20	0	0	0
	Concentrated	40	0	0	0
	Diluted	40	0	0	0

* The mean for cracks = 0.008
† The mean for smooth = 0.008

TABLE 7.9

Comparison of the defects per unit area on the surface of PVC gloves following exposure to a malathion based insecticide on the 10/5/95. The samples were covered, exposed, treated with concentrated insecticide or diluted insecticide. (Dunn's method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		**Treatment**			
		Covered	Exposed	Concentrated	Diluted
Cavities	Covered				
	Exposed	NS			
	Concentrated	NS	NS		
	Diluted	<0.05	<0.05	<0.05	
Contaminants	Covered				
	Exposed	NS			
	Concentrated	NS	NS		
	Diluted	<0.05	NS	<0.05	
Convexities	Covered				
	Exposed	NS			
	Concentrated	NS	NS		
	Diluted	NS	<0.05	<0.05	

7.3.2 Short-term exposures: nitrile-butadiene rubber

These experiments are presented by dates and the insecticides used.

7.3.2.1 Sol-Vex™ gloves exposed to weathering on the 6/4/95 and Top Clip Blue Shield®

The data are summarised in Tables 7.10 and 7.11. There were no differences for cracks between the treatments (H = 7.30, d.f. = 3, P = 0.0629). Cavities differed strongly between treatments (H = 43.8, d.f. = 3, P <0.0001). Convexities also differed strongly between treatments (H = 36.1, d.f. = 3, P <0.0001). Smooth areas did not differ between treatments (H = 2.82, d.f. = 3, P = 0.420). Slumps varied strongly between treatments (H = 76.4, d.f. = 3, P <0.0001). Contaminants also differed (H = 10.7, d.f. = 3, P = 0.0133).

TABLE 7.10

Defects per unit area on the surface of Sol-Vex™ gloves following exposure to the outdoor environment and Top Clip Blue Shield® on the 6/4/95. The samples were covered, exposed, treated with concentrated or diluted insecticide. (Kruskal-Wallis One Way ANOVA on Ranks.)

Defects	Treatment	n	Median	25%	75%
Cavities	Covered	10	1	1	1
	Exposed	20	3	2	4
	Concentrated	50	3	2	4
	Diluted	40	5	4	6
Contaminants	Covered	10	0	0	0
	Exposed	20	0	0	0
	Concentrated	50	0	0	2
	Diluted	40	0	0	1
Convexities	Covered	10	0	0	0
	Exposed	20	2	0	3
	Concentrated	50	2	1	3
	Diluted	40	5	2	6
Cracks*	Covered	10	0	0	0
	Exposed	20	0	0	0
	Concentrated	50	0	0	0
	Diluted	40	0	0	0
Slumps	Covered	10	2	1	3
	Exposed	20	1	0	2
	Concentrated	50	0	0	1
	Diluted	40	0	0	0
Smooth†	Covered	10	0	0	0
	Exposed	20	0	0	0
	Concentrated	50	0	0	0
	Diluted	40	0	0	0

* The mean for cracks = 0.283
† The mean for smooth = 0.016

TABLE 7.11

Comparison of the defects per unit area on the surface of Sol-Vex™ gloves following exposure to a diazinon based insecticide on the 6/4/95. The samples were covered, exposed, treated with concentrated or diluted insecticide. (Dunn's method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		**Treatment**			
		Covered	Exposed	Concentrated	Diluted
Cavities	Covered				
	Exposed	NS			
	Concentrated	NS	NS		
	Diluted	<0.05	<0.05	<0.05	
Contaminants	Covered				
	Exposed	NS			
	Concentrated	<0.05	NS		
	Diluted	NS	NS	NS	
Convexities	Covered				
	Exposed	NS			
	Concentrated	<0.05	NS		
	Diluted	<0.05	<0.05	<0.05	
Slumps	Covered				
	Exposed	<0.05			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	NS	

7.3.2.2 Sol-Vex™ gloves exposed to weathering on the 28/4/95 and Top Clip Blue Shield®

Cracks varied strongly between treatments (H = 87.6, d.f. = 3, P <0.001). Cavities varied between treatments, but not as strongly (H = 10.2, d.f. = 3, P = 0.0169). Convexities differed between treatments (H = 22.3, d.f. = 3, P <0.0001). There were very few smooth areas on these samples and they did not differ between treatments (H = 5.38, d.f. = 3, P = 0.1458). Slumps differed between treatments (H = 10.0, d.f. = 3, P = 0.0186). There were no differences for contaminants between treatments (H = 2.79, d.f. = 3, P = 0.4246). The data are summarised in Tables 7.12 and 7.13.

TABLE 7.12

Defects per unit area on the surface of Sol-Vex™ gloves following exposure to the outdoor environment and Top Clip Blue Shield® on the 28/4/95. The samples were covered, exposed, treated with concentrated or diluted insecticide. The medians, 25th and 75th percentiles are shown. (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatment	n	Median	25%	75%
Cavities	Covered	20	4	3	4
	Exposed	10	4	2	4
	Concentrated	30	3	1	4
	Diluted	50	4	3	5
Contaminants*	Covered	20	0	0	0
	Exposed	10	0	0	0
	Concentrated	30	0	0	0
	Diluted	50	0	0	0
Convexities	Covered	20	4	2	4
	Exposed	10	2	0	2
	Concentrated	30	3	2	3
	Diluted	50	4	3	5
Cracks	Covered	20	0	0	0
	Exposed	10	6	4	6
	Concentrated	30	0	0	0
	Diluted	50	0	0	0
Slumps†	Covered	20	0	0	0
	Exposed	10	0	0	0
	Concentrated	30	0	0	0
	Diluted	50	0	0	0
Smooth§	Covered	20	0	0	0
	Exposed	10	0	0	0
	Concentrated	30	0	0	0
	Diluted	50	0	0	0

* The mean for contaminants = 0.2
† The mean for slumps = 0.009
§ The mean for smooth = 0.018

TABLE 7.13

Comparison of the defects per unit area on the surface of Sol-Vex™ gloves following exposure to a diazinon based insecticide on the 28/4/95. The samples were covered, exposed, treated with concentrated or diluted insecticide. (Dunn's method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		**Treatment**			
		Covered	Exposed	Concentrated	Diluted
Cavities	Covered				
	Exposed	NS			
	Concentrated	NS	NS		
	Diluted	NS	NS	<0.05	
Convexities	Covered				
	Exposed	NS			
	Concentrated	NS	NS		
	Diluted	NS	<0.05	<0.05	
Cracks	Covered				
	Exposed	<0.05			
	Concentrated	NS	<0.05		
	Diluted	NS	<0.05	NS	
Slumps	Covered				
	Exposed	<0.05			
	Concentrated	NS	<0.05		
	Diluted	NS	<0.05	NS	

7.3.2.3 Sol-Vex™ gloves exposed to weathering on the 10/5/95 and Lorsban®

There were differences for cracks between treatments (H = 19.6, d.f. = 3, P = 0.0002). Cavities also differed between treatments (H = 20.5, d.f. = 3, P = 0.0001). Convexities differed more strongly between treatments (H = 32.8, d.f. = 3, P <0.0001). There were very few smooth areas and consequently there were no differences between treatments (H = 1.80, d.f. = 3, P = 0.165). Slumps differed between treatments (H = 12.1, d.f. = 3, P = 0.0071). There were no differences between treatments for contaminants (H = 5.09, d.f. = 3, P = 0.1656). The data are summarised in Tables 7.14 and 7.15.

TABLE 7.14

Defects per unit area on the surface of Sol-Vex™ gloves following exposure to the outdoor environment and Lorsban® on the 10/5/95. The samples were either covered, exposed, treated with concentrated or diluted insecticide. The medians, 25th and 75th percentiles are shown. (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatment	n	Median	25%	75%
Cavities	Covered	20	4	3	5
	Exposed	20	4	3	4
	Concentrated	50	5	4	8
	Diluted	50	3	2	4
Contaminants	Covered	20	0	0	0
	Exposed	20	0	0	0
	Concentrated	50	0	0	1
	Diluted	50	0	0	0
Convexities	Covered	20	3	2	4
	Exposed	20	2	1	3
	Concentrated	50	5	3	7
	Diluted	50	3	0	4
Cracks	Covered	20	0	0	0
	Exposed	20	0	0	0
	Concentrated	50	0	0	0
	Diluted	50	0	0	1
Slumps*	Covered	20	0	0	0
	Exposed	20	0	0	0
	Concentrated	50	0	0	0
	Diluted	50	0	0	0
Smooth†	Covered	20	0	0	0
	Exposed	20	0	0	0
	Concentrated	50	0	0	0
	Diluted	50	0	0	0

* The mean for slumps = 0.007
† The mean for smooth = 0.021

TABLE 7.15

Comparison of the defects per unit area on the surface of Sol-Vex™ gloves following exposure to a chlorpyrifos based insecticide on the 10/5/95. The samples were either covered, exposed, treated with concentrated or diluted insecticide. (Dunn's method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		**Treatment**			
		Covered	Exposed	Concentrated	Diluted
Cavities	Covered				
	Exposed	NS			
	Concentrated	NS	<0.5		
	Diluted	NS	NS	<0.05	
Convexities	Covered				
	Exposed	NS			
	Concentrated	NS	<0.05		
	Diluted	NS	NS	<0.05	
Cracks	Covered				
	Exposed	NS			
	Concentrated	NS	NS		
	Diluted	<0.05	<0.05	<0.05	
Slumps	Covered				
	Exposed	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	NS	NS	

7.3.2.4 Sol-Vex™ gloves exposed to weathering on the 10/5/95 and Malathion®

Cracks differed between treatments (H = 11.2, d.f. = 3, P = 0.0107). Cavities differed between treatments, but not as strongly as for cracks (H = 8.28, d.f. = 3, P = 0.0406). Convexities differed between treatments (H = 13, d.f. = 3, P = 0.0047). Smooth areas did not differ between treatments (H = 4.03, d.f. = 3, P = 0.2578). Slumps differed between treatments (H = 10.1, d.f. = 3, P = 0.0179). There were differences for contaminants (H = 10.1, d.f. = 3, P = 0.0179). The data are summarised in Tables 7.16 and 7.17.

TABLE 7.16

Defects per unit area on the surface of Sol-Vex™ gloves following exposure to the outdoor environment and Malathion® on the 10/5/95. The samples were either covered, exposed, treated with concentrated or diluted insecticide. The medians, 25th and 75th percentiles are shown. (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatment	n	Median	25%	75%
Cavities	Covered	20	4	3	5
	Exposed	20	4	3	4
	Concentrated	40	4	3	5
	Diluted	40	3	2	4
Contaminants*	Covered	20	0	0	0
	Exposed	20	0	0	0
	Concentrated	40	0	0	0
	Diluted	40	0	0	0
Convexities	Covered	20	3	2	4
	Exposed	20	2	1	3
	Concentrated	40	4	3	5
	Diluted	40	3	1	5
Cracks	Covered	20	0	0	0
	Exposed	20	0	0	0
	Concentrated	40	0	0	0
	Diluted	40	0	0	1
Slumps†	Covered	20	0	0	0
	Exposed	20	0	0	0
	Concentrated	40	0	0	0
	Diluted	40	0	0	0
Smooth§	Covered	20	0	0	0
	Exposed	20	0	0	0
	Concentrated	40	0	0	0
	Diluted	40	0	0	0

* The mean for contaminants = 0.289
† The mean for slumps = 0.025 (all the counts were in the covered samples)
§ The mean for smooth = 0.017

TABLE 7.17

Comparison of defects per unit area on the surface of Sol-Vex™ gloves following exposure to Malathion® on the 10/5/95. The samples were either covered, exposed, treated with concentrated or diluted insecticide (Dunn's method following Kruskal-Wallis One Way ANOVA on Ranks). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		**Treatment**			
		Covered	Exposed	Concentrated	Diluted
Cavities	Covered				
	Exposed	NS			
	Concentrated	NS	NS		
	Diluted	NS	NS	<0.05	
Contaminants	Covered				
	Exposed	NS			
	Concentrated	<0.05	NS		
	Diluted	<0.05	NS	NS	
Convexities	Covered				
	Exposed	NS			
	Concentrated	NS	<0.05		
	Diluted	NS	NS	<0.05	
Cracks	Covered				
	Exposed	NS			
	Concentrated	NS	NS		
	Diluted	<0.05	NS	NS	
Slumps	Covered				
	Exposed	NS			
	Concentrated	<0.05	NS		
	Diluted	<0.05	NS	NS	

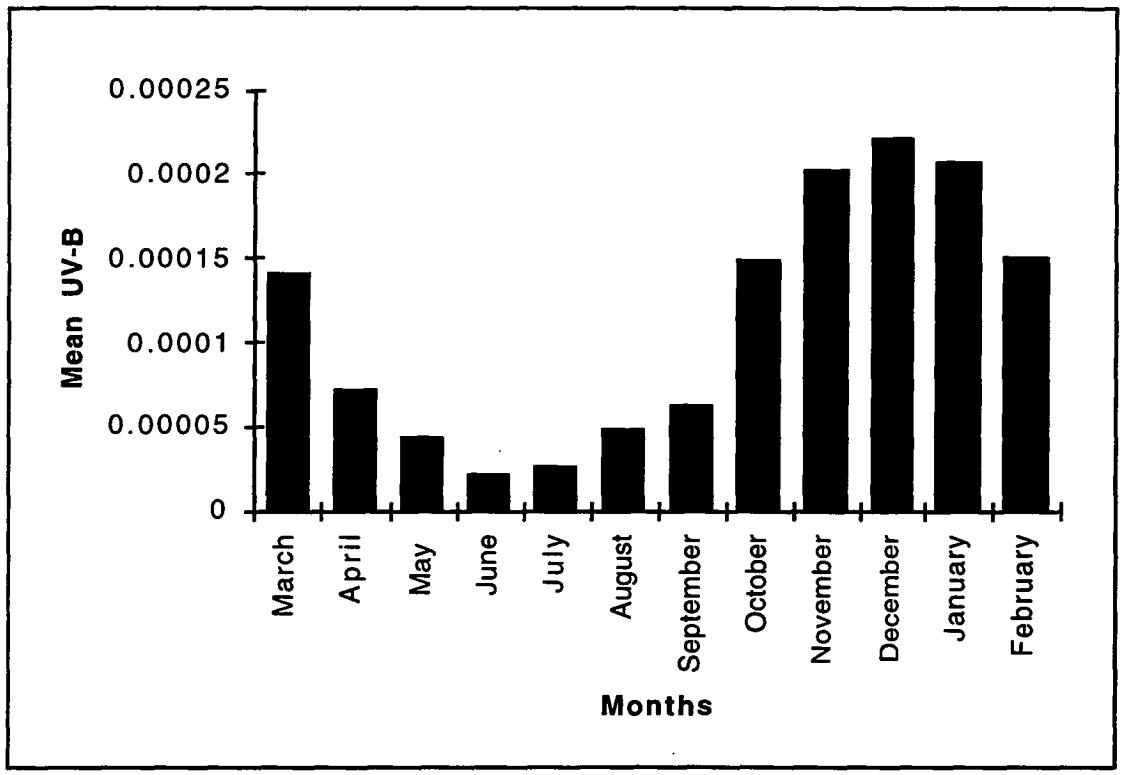
7.3.3 Long-term exposures: polyvinyl chloride

The glove specimens were taken at monthly intervals until visible dissociation occurred. A general narrative account is given for the visible and microscopic defects at the beginning of the PVC and NBR sections below. The results from the defect analyses are presented before the results from the X-ray microanalyses, and are arranged under monthly headings. Polyvinyl chloride is described before NBR.

The mean monthly UV recordings from the experimental site are shown in Figure 7.1.

FIGURE 7.1

Mean monthly ultraviolet B radiation (kJ/m^2) from 1/3/95-29/2/96



7.3.3.1 Narrative account of visible and microscopic defects: polyvinyl chloride

At four months some parts of some of the PVC gloves became sticky and particulates became attached. From five months onwards there was a progressive visible dissociation. This was accompanied by some colour changes, the red changing to yellow and brown in blotchy raised areas. These areas were circumscribed and were very sticky (Figure 7.2).

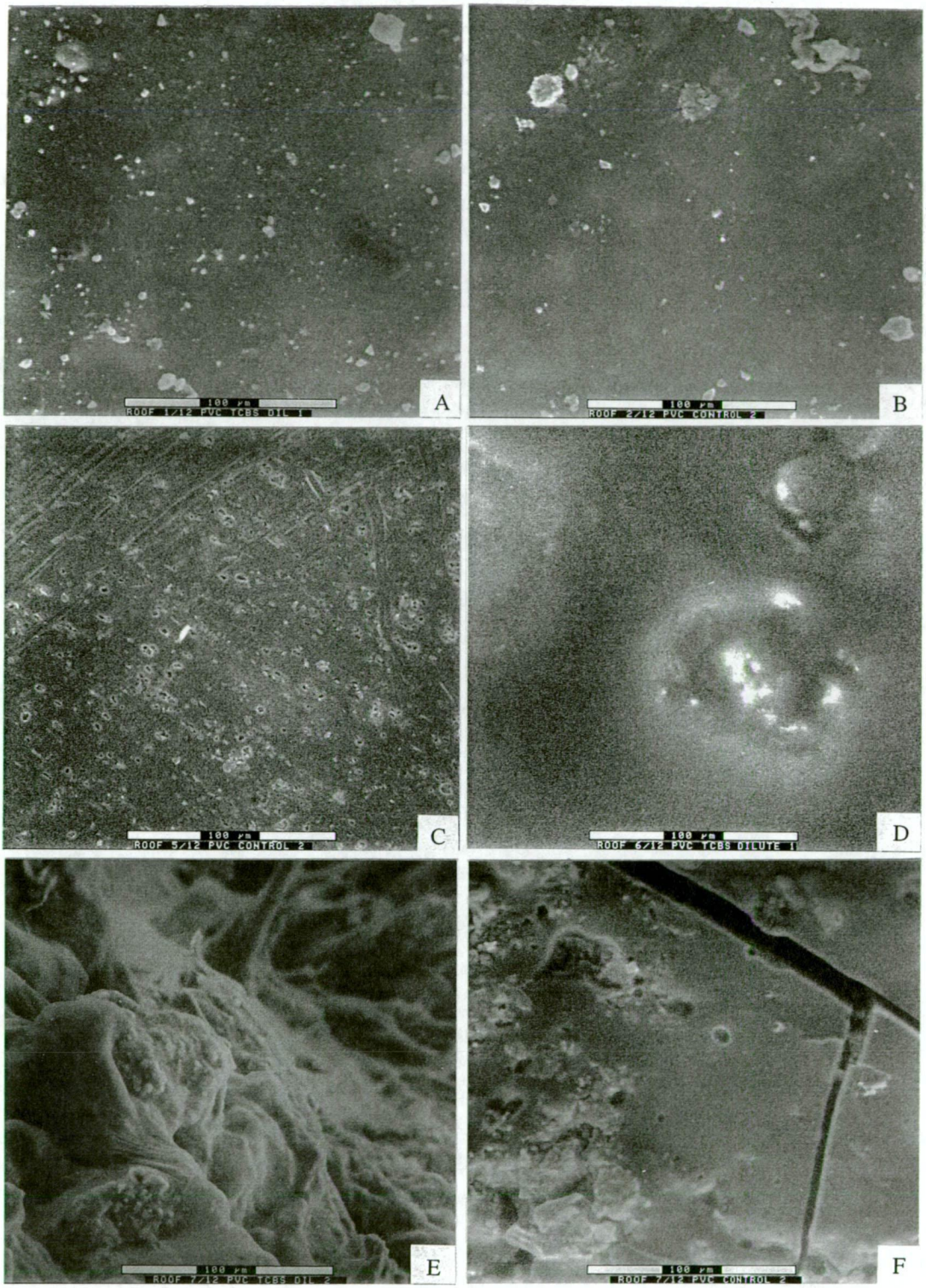
Microscopically, after one month all the PVC samples generally had a wavy undulating appearance with some distinctive domains, or convexities. This pattern remained fairly characteristic until five months exposure, when the untreated sample lost the domains and had an etched appearance. At six and seven months, the effects of dissociation became apparent, the surface was very uneven and there were significant structural changes. A few cracks were observed in PVC after four months exposure. The cracks from four to five months were very fine and the surface topography had an etched appearance. At six and seven months the cracks were much larger, straight and had angular branches similar to those in the freeze fracture micrograph of the PVC that had been fractured outside the liquid nitrogen container. Figure 7.3 contains a chronological illustration of PVC long-term exposures.

FIGURE 7.2

Dissociation of PVC following seven months outdoor exposure

FIGURE 7.3

Environmental scanning electron micrographs (400 x) detailing changes in PVC gloves following outdoor exposure



A: PVC following exposure to weather and dilute Top Clip Blue Shield® for 1 month, showing contaminants and convexities. B: PVC following exposure to weather for 2 months, showing contaminants and convexities. C: PVC following exposure to weather for 5 months, showing an etched surface with cavities. D: PVC following exposure to weather and dilute Top Clip Blue Shield® for 6 months, showing convexities and cavities. E: PVC following exposure to weather and dilute Top Clip Blue Shield® for 7 months, showing dissociation. F: PVC following exposure to weather for 7 months, showing cavities and brittle fractures.

7.3.3.1 Defects following exposure for one month

There were no cracks in the PVC samples for this exposure period. There were differences for cavities between the treatments ($H = 45.3$, d.f. = 3, $P < 0.0001$). Convexities differed between treatments ($H = 42.0$, d.f. = 3, $P < 0.0001$). Smooth areas did not differ between treatments ($H = 3$, d.f. = 3, $P = 0.392$). Contaminants varied between treatments ($H = 8.30$, d.f. = 3, $P = 0.0402$). The data are presented in Tables 7.18 and 7.19.

TABLE 7.18

Defects per unit area on the surface of PVC gloves following exposure to the outdoor environment for one month and concentrated or diluted Top Clip Blue Shield®. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatment	n	Median	25%	75%
Cavities	New	20	8	7	9
	Untreated	20	3	2	4
	Concentrated	20	3	3	4
	Diluted	20	2	2	3
Contaminants	New	20	0	0	1
	Untreated	20	2	0	2
	Concentrated	20	2	0	4
	Diluted	20	3	0	8
Convexities	New	20	7	6	8
	Untreated	20	3	2	4
	Concentrated	20	0	0	2
	Diluted	20	2	1	3
Smooth*	New	20	0	0	0
	Untreated	20	0	0	0
	Concentrated	20	0	0	0
	Diluted	20	0	0	0

* The mean for smooth = 0.013

TABLE 7.19

Comparison of the defects per unit area on the surface of PVC gloves following exposure to Top Clip Blue Shield® and weather for one month. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		**Treatments**			
		New	Untreated	Concentrated	Diluted
Cavities	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	NS	NS	
Contaminants	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	NS	NS	
Convexities	New				
	Untreated	<0.05			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	<0.05	

7.3.3.2 X-ray microanalysis following one month exposure

There were no differences for carbon between treatments ($F_{3,14} = 0.807$, P = 0.5106). Oxygen concentrations differed between treatments ($F_{3,14} = 11.6$, P = 0.0004). There were no variations for aluminium between treatments (H = 6.65, d.f. = 3, P = 0.0840). There were variations for silicon (H = 15.6, d.f. = 3, P = 0.0013). Phosphorus differed between treatments (H = 12.2, d.f. = 3, P = 0.0067). Sulfur differed strongly between treatments ($F_{3,14} = 43.8$, P <0.0001). There were no variations for chlorine between treatments ($F_{3,14} = 0.518$, P = 0.677). The data are presented in Tables 7.20 and 7.21.

TABLE 7.20

Elements (counts per second) on the surface of PVC gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for one month. The medians, 25th and 75th percentiles are shown for the abnormal distributions (Kruskal-Wallis One Way ANOVA on Ranks). The means and standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Treatment	n	Median	25%	75%
Aluminium	New	6	424	387	624
	Untreated	6	506	468	556
	Concentrated	3	897	720	1835
	Diluted	3	783	772	809
Silicon	New	6	431	345	522
	Untreated	6	1069	984	1098
	Concentrated	3	1963	1750	2079
	Diluted	3	2198	2151	3736
Phosphorus	New	6	0	0	0
	Untreated	6	0	0	0
	Concentrated	3	0	0	22
	Diluted	3	178	148	243
				Mean ± se	
Carbon	New	6		7577 ± 717	
	Untreated	6		8966 ± 712	
	Concentrated	3		8275 ± 588	
	Diluted	3		8361 ± 378	
Oxygen	New	6		6264 ± 517	
	Untreated	6		11234 ± 903	
	Concentrated	3		10177 ± 692	
	Diluted	3		11907 ± 883	
Sulfur	New	6		378 ± 23	
	Untreated	6		473 ± 26	
	Concentrated	3		394 ± 11	
	Diluted	3		791 ± 23	
Chlorine	New	6		33321 ± 1731	
	Untreated	6		35633 ± 1937	
	Concentrated	3		33663 ± 825	
	Diluted	3		32640 ± 1602	

TABLE 7.21

Comparison of the elements per unit area on the surface of PVC gloves following exposure to Top Clip Blue Shield® and weather for one month (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or Dunn's method following One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		**Treatments**			
		New	Untreated	Concentrated	Diluted
Oxygen	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	NS	NS	
Silicon	New				
	Untreated	NS			
	Concentrated	<0.05	NS		
	Diluted	<0.05	NS	NS	
Phosphorus	New				
	Untreated	NS			
	Concentrated	NS	NS		
	Diluted	<0.05	<0.05	NS	
Sulfur	New				
	Untreated	<0.05			
	Concentrated	NS	NS		
	Diluted	<0.05	<0.05	<0.05	

7.3.3.3 Defects following exposure for two months

There were no cracks or smooth areas on the PVC samples for this exposure period. Cavities differed strongly between treatments ($H = 46.4$, d.f. = 3, $P < 0.0001$). Convexities also differed strongly between treatments ($H = 46.2$, d.f. = 3, $P < 0.0001$). Contaminants varied between treatments ($H = 36.4$, d.f. = 3, $P < 0.0001$). The data are summarised in Tables 7.22 and 7.23.

TABLE 7.22

Defects per unit area on the surface of PVC gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for two months. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatment	n	Median	25%	75%
Cavities	New PVC	20	8	7	9
	Untreated PVC	20	2	1	4
	Concentrated	20	3	2	3
	Diluted	20	4	3	4
Contaminants	New PVC	20	0	0	1
	Untreated PVC	20	3	2	5
	Concentrated	20	2	1	3
	Diluted	20	0	0	0
Convexities	New PVC	20	7	6	8
	Untreated PVC	20	2	1	2
	Concentrated	20	2	1	2
	Diluted	20	3	3	4

TABLE 7.23

Comparison of the defects per unit area on the surface of PVC gloves following exposure to Top Clip Blue Shield® and weather for two months. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		Treatments			
		New	Untreated	Concentrated	Diluted
Cavities	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	<0.05	NS	
Contaminants	New				
	Untreated	<0.05			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	<0.05	
Convexities	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	<0.05	<0.05	

7.3.3.4 X-ray microanalysis following two months exposure

There were no differences for carbon between treatments (H = 6.46, d.f. = 3, P = 0.0913). Oxygen varied between treatments ($F_{3,11}$ = 12.3, P = 0.0008). Aluminium varied between treatments, but the power of the performed test was slightly below the desired power ($F_{3,11}$ = 5.25, P = 0.0172). There were variations for silicon (H = 11.4, d.f. = 3, P = 0.0096). Phosphorus differed between treatments (H = 9.58, d.f. = 3, P = 0.0225), as did sulfur ($F_{3,11}$ = 4.89, P = 0.0213). There were no differences for chlorine between treatments ($F_{3,11}$ = 1.21, P = 0.353). The data are summarised in Tables 7.24 and 7.25.

TABLE 7.24

Elements (counts per second) on the surface of PVC gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for two months. The medians, 25th and 75th percentiles are shown for the abnormal distributions (Kruskal-Wallis One Way ANOVA on Ranks). The means and standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Treatment	n	Median	25%	75%
Carbon	New	6	6600	6515	8744
	Untreated	3	8097	7964	11804
	Concentrated	3	7324	5993	11451
	Diluted	3	12890	12074	71039
Silicon	New	6	431	345	522
	Untreated	3	1700	1334	2348
	Concentrated	3	1083	902	1465
	Diluted	3	1149	1112	1265
Phosphorus	New	6	0	0	0
	Untreated	3	0	0	2
	Concentrated	3	149	42	165
	Diluted	3	0	0	69
				Mean ± se	
Oxygen	New	6		6264 ± 517	
	Untreated	3		10851 ± 581	
	Concentrated	3		8063 ± 1260	
	Diluted	3		11676 ± 755	
Aluminium	New	6		549 ± 116	
	Untreated	3		1063 ±112	
	Concentrated	3		454 ± 93	
	Diluted	3		440 ± 63	
Sulfur	New	6		378 ± 23	
	Untreated	3		603 ± 131	
	Concentrated	3		636 ± 44	
	Diluted	3		423 ± 46	
Chlorine	New	6		33321 ± 1731	
	Untreated	3		39218 ± 646	
	Concentrated	3		36084 ± 4546	
	Diluted	3		37023 ± 1658	

TABLE 7.25

Comparison of the elements per unit area on the surface of PVC gloves following exposure to Top Clip Blue Shield® and weather for two months (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or Dunn's method following One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		**Treatments**			
		New	Untreated	Concentrated	Diluted
Oxygen	New				
	Untreated	<0.05			
	Concentrated	NS	<0.05		
	Diluted	<0.05	NS	<0.05	
Aluminium	New				
	Untreated	<0.05			
	Concentrated	NS	<0.05		
	Diluted	NS	<0.05	NS	
Silicon	New				
	Untreated	<0.05			
	Concentrated	NS	NS		
	Diluted	NS	NS	NS	
Phosphorus	New				
	Untreated	NS			
	Concentrated	<0.05	NS		
	Diluted	NS	NS	NS	
Sulfur	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	NS	NS	NS	

7.3.3.5 Defects following exposure for three months

There were no cracks or smooth areas for this exposure period. Cavities differed between treatments ($H = 37.6$, d.f. = 3, $P < 0.0001$). Convexities differed between treatments ($H = 14.5$, d.f. = 3, $P = 0.0023$). There were differences for contaminants between treatments ($H = 27.3$, d.f. = 3, $P < 0.0001$). A summary of the data is presented in Tables 7.26 and 7.27.

TABLE 7.26

Defects per unit area on the surface of PVC gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for three months. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatment	n	Median	25%	75%
Cavities	New PVC	20	8	7	9
	Untreated PVC	20	6	5	7
	Concentrated	20	4	4	4
	Diluted	20	4	3	6
Contaminants	New PVC	20	0	0	1
	Untreated PVC	20	5	1	8
	Concentrated	20	5	4	6
	Diluted	20	3	2	4
Convexities	New PVC	20	7	6	8
	Untreated PVC	20	5	3	6
	Concentrated	20	4	2	7
	Diluted	20	5	5	8

TABLE 7.27

Comparison of the defects per unit area on the surface of PVC gloves following exposure to Top Clip Blue Shield® and weather for three months. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		**Treatments**			
		New	Untreated	Concentrated	Diluted
Cavities	New				
	Untreated	<0.05			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	NS	
Contaminants	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	<0.05	<0.05	
Convexities	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	NS	<0.05	<0.05	

7.3.3.6 X-ray microanalysis following exposure for three months

There were differences for carbon between treatments (H = 8.80, d.f. = 3, P = 0.0321). Oxygen varied between treatments (H = 9.23, d.f. = 3, P = 0.0264). There were no variations for aluminium ($F_{3,11}$ = 2.44, P = 0.119). Silicon varied between treatments ($F_{3,11}$ = 17.3, P = 0.0002). Phosphorus differed between treatments (H = 11.9, d.f. = 3, P = 0.0079). There were marked differences for sulphur between treatments ($F_{3,11}$ = 31, P <0.0001). Chlorine did not vary between treatments (H = 6.83, d.f. = 3, P = 0.0777). Tables 7.28 and 7.29 contain a summary of the data.

TABLE 7.28

Elements (counts per second) on the surface of PVC gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for three months. The medians, 25th and 75th percentiles are shown for the abnormal distributions (Kruskal-Wallis One Way ANOVA on Ranks). The means and standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Treatment	n	Median	25%	75%
Carbon	New	6	6600	6515	8744
	Untreated	3	8826	8456	9116
	Concentrated	3	7344	6599	7490
	Diluted	3	10903	10815	11247
Oxygen	New	6	6025	5210	7360
	Untreated	3	10198	3376	10949
	Concentrated	3	9056	8976	9757
	Diluted	3	12066	11593	12187
Phosphorus	New	6	0	0	0
	Untreated	3	0	0	14
	Concentrated	3	300	291	335
	Diluted	3	0	0	0
Chlorine	New	6	31900	30236	34480
	Untreated	3	38306	35439	38781
	Concentrated	3	32627	31630	33934
	Diluted	3	40486	39696	41069
				Mean ± se	
Aluminium	New	6		549 ± 116	
	Untreated	3		627 ± 8	
	Concentrated	3		1022 ± 194	
	Diluted	3		842 ± 160	
Silicon	New	6		433 ± 72	
	Untreated	3		1859 ± 564	
	Concentrated	3		2806 ± 282	
	Diluted	3		1396 ± 73	
Sulfur	New	6		378 ± 23	
	Untreated	3		479 ± 52	
	Concentrated	3		807 ± 23	
	Diluted	3		467 ± 41	

TABLE 7.29

Comparison of the elements per unit area on the surface of PVC gloves following exposure to Top Clip Blue Shield® and weather for three months (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or Dunn's method following One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		**Treatments**			
		New	Untreated	Concentrated	Diluted
Carbon	New				
	Untreated	NS			
	Concentrated	NS	NS		
	Diluted	NS	NS	NS	
Oxygen	New				
	Untreated	NS			
	Concentrated	NS	NS		
	Diluted	<0.05	NS	NS	
Silicon	New				
	Untreated	<0.05			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	NS	<0.05	
Phosphorus	New				
	Untreated	NS			
	Concentrated	<0.05	NS		
	Diluted	NS	NS	<0.05	
Sulfur	New				
	Untreated	NS			
	Concentrated	<0.05	<0.05		
	Diluted	NS	NS	<0.05	

7.3.3.7 Defects following exposure for four months

There were no smooth areas on the PVC samples for this exposure period. There were no differences between treatments for cracks (H = 3, d.f. = 3, P = 0.392). Cavities differed strongly between treatments (H = 30, d.f. = 3, P <0.0001). There were strong differences for convexities between treatments (H = 39.3, d.f. = 3, P <0.0001). Contaminants differed strongly between treatments (H = 33.9, d.f. = 3, P <0.0001). A summary of the data is presented in Tables 7.30 and 7.31.

TABLE 7.30

Defects per unit area on the surface of PVC gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for four months. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatment	n	Median	25%	75%
Cavities	New PVC	20	8	7	9
	Untreated PVC	20	7	5	10
	Concentrated	20	4	3	6
	Diluted	20	4	4	5
Contaminants	New PVC	20	0	0	1
	Untreated PVC	20	9	6	12
	Concentrated	20	3	2	4
	Diluted	20	4	2	6
Convexities	New PVC	20	7	6	8
	Untreated PVC	20	0	0	3
	Concentrated	20	3	2	5
	Diluted	20	4	3	5
Cracks*	New PVC	20	0	0	0
	Untreated PVC	20	0	0	0
	Concentrated	20	0	0	0
	Diluted	20	0	0	0

* The mean for cracks = 0.025

TABLE 7.31

Comparison of the defects per unit area on the surface of PVC gloves following exposure to Top Clip Blue Shield® and weather for four months. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		Treatments			
		New	Untreated	Concentrated	Diluted
Cavities	New				
	Untreated	<0.05			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	NS	
Contaminants	New				
	Untreated	<0.05			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	NS	
Convexities	New				
	Untreated	<0.05			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	NS	

7.3.3.8 X-ray microanalysis following exposure for four months

There were no differences for carbon between treatments ($F_{3,11} = 1.95$, $P = 0.181$). There were differences for oxygen between treatments ($H = 9.40$, d.f. = 3, $P = 0.0244$). Aluminium varied between treatments ($F_{3,11} = 10$, $P = 0.0018$). There were variations for silicon concentrations between treatments ($H = 12.6$, d.f. = 3, $P = 0.0057$). Phosphorus varied between treatments ($H = 13.8$, d.f. = 3, $P = 0.0032$). Sulfur varied strongly between treatments ($F_{3,11} = 32.3$, $P < 0.0001$). Chlorine did not vary ($F_{3,11} = 1.31$, $P = 0.3194$). Tables 7.32 and 7.33 contain a summary of the data.

TABLE 7.32

Elements (counts per second) on the surface of PVC gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for four months. The medians, 25th and 75th percentiles are shown for the abnormal distributions (Kruskal-Wallis One Way ANOVA on Ranks). The means and standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Treatment	n	Median	25%	75%
Oxygen	New	6	6025	5210	7360
	Untreated	3	13357	9375	16689
	Concentrated	3	12392	11347	12812
	Diluted	3	6866	6698	8319
Silicon	New	6	431	345	522
	Untreated	3	2945	2238	3502
	Concentrated	3	1998	1590	2513
	Diluted	3	951	839	1295
Phosphorus	New	6	0	0	0
	Untreated	3	0	0	0
	Concentrated	3	337	279	374
	Diluted	3	0	0	0
				Mean ± se	
Carbon	New	6	7577 ± 717		
	Untreated	3	10404 ± 2300		
	Concentrated	3	10428 ± 394		
	Diluted	3	7651 ± 973		
Aluminium	New	6	549 ± 116		
	Untreated	3	1305 ± 147		
	Concentrated	3	947 ± 62		
	Diluted	3	426 ± 66		
Sulfur	New	6	378 ± 23		
	Untreated	3	753 ± 88		
	Concentrated	3	929 ± 50		
	Diluted	3	999 ± 85		
Chlorine	New	6	33321 ± 1731		
	Untreated	3	31983 ± 671		
	Concentrated	3	33765 ± 39		
	Diluted	3	29215 ± 1294		

TABLE 7.33

Comparison of the elements per unit area on the surface of PVC gloves following exposure to Top Clip Blue Shield® and weather for four months (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or Dunn's method following One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		**Treatments**			
		New	Untreated	Concentrated	Diluted
Oxygen	New				
	Untreated	NS			
	Concentrated	NS	NS		
	Diluted	NS	NS	NS	
Aluminium	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	NS	<0.05	<0.05	
Silicon	New				
	Untreated	<0.05			
	Concentrated	NS	NS		
	Diluted	NS	NS	NS	
Phosphorus	New				
	Untreated	NS			
	Concentrated	<0.05	<0.05		
	Diluted	NS	NS	<0.05	
Sulfur	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	<0.05	NS	

7.3.3.9 Defects following exposure for five months

There were no smooth areas for this exposure period. Cracks did not differ between treatments (H = 6.08, d.f. = 3, P = 0.108). Cavities differed between treatments (H = 16.5, d.f. = 3, P = 0.0009). Convexities differed strongly between treatments (H = 28, d.f. = 3, P <0.0001). There were strong variations for contaminants between treatments (H = 27.1, d.f. = 3, P <0.0001). The data are summarised in Tables 7.34 and 7.35.

TABLE 7.34

Defects per unit area on the surface of PVC gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for five months (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatment	n	Median	25%	75%
Cavities	New PVC	20	8	7	9
	Untreated PVC	20	7	4	10
	Concentrated	20	5	4	6
	Diluted	20	5	4	7
Contaminants	New PVC	20	0	0	1
	Untreated PVC	20	4	0	13
	Concentrated	20	3	0	5
	Diluted	20	11	5	15
Convexities	New PVC	20	7	6	8
	Untreated PVC	20	1	0	3
	Concentrated	20	4	3	7
	Diluted	20	3	2	4
Cracks*	New PVC	20	0	0	0
	Untreated PVC	20	0	0	0
	Concentrated	20	0	0	0
	Diluted	20	0	0	0

* The mean for cracks = 0.025

TABLE 7.35

Comparison of the defects per unit area on the surface of PVC gloves following exposure to Top Clip Blue Shield® and weather for five months. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		**Treatments**			
		New	Untreated	Concentrated	Diluted
Cavities	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	NS	NS	
Contaminants	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	<0.05	<0.05	
Convexities	New				
	Untreated	<0.05			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	<0.05	

7.3.3.10 X-ray microanalysis following exposure for five months

Carbon did not vary between treatments ($H = 4.43$, d.f. = 3, $P = 0.2191$). There were differences for oxygen ($F_{3,11} = 8.01$, $P = 0.0041$). Aluminium varied between treatments ($F_{3,11} = 8.47$, $P = 0.0034$), as did silicon ($H = 12.4$, d.f. = 3, $P = 0.0063$). There were differences for phosphorus ($H = 10.5$, d.f. = 3, $P = 0.0149$) and sulfur ($H = 12.2$, d.f. = 3, $P = 0.0068$). Chlorine did not differ ($F_{3,11} = 2.63$, $P = 0.1025$). A summary of the data is presented in Tables 7.36 and 7.37.

TABLE 7.36

Elements (counts per second) on the surface of PVC gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for five months. The medians, 25th and 75th percentiles are shown for the abnormal distributions (Kruskal-Wallis One Way ANOVA on Ranks). The means and standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Treatment	n	Median	25%	75%
Carbon	New	6	6600	6515	8744
	Untreated	3	4893	4099	9695
	Concentrated	3	9506	8986	12259
	Diluted	3	7291	6372	7572
Silicon	New	6	431	345	522
	Untreated	3	6789	6485	7548
	Concentrated	3	2483	1828	3958
	Diluted	3	1595	1171	2449
Phosphorus	New	6	0	0	0
	Untreated	3	0	0	74
	Concentrated	3	177	134	330
	Diluted	3	48	12	65
Sulfur	New	6	365	337	394
	Untreated	3	1760	1175	2078
	Concentrated	3	565	565	734
	Diluted	3	591	566	636
				Mean ± se	
Oxygen	New	6		6264 ± 517	
	Untreated	3		16134 ± 3627	
	Concentrated	3		10970 ± 866	
	Diluted	3		8337 ± 650	
Aluminium	New	6		549 ± 116	
	Untreated	3		2614 ± 549	
	Concentrated	3		1700 ± 582	
	Diluted	3		687 ± 140	
Chlorine	New	6		33321 ± 1731	
	Untreated	3		27483 ± 5575	
	Concentrated	3		24011 ± 1201	
	Diluted	3		27062 ± 341	

TABLE 7.37

Comparison of the elements per unit area on the surface of PVC gloves following exposure to Top Clip Blue Shield® and weather for five months (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or Dunn's method following One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		Treatments			
		New	Untreated	Concentrated	Diluted
Oxygen	New				
	Untreated	<0.05			
	Concentrated	NS	NS		
	Diluted	NS	<0.05	NS	
Aluminium	New				
	Untreated	<0.05			
	Concentrated	NS	NS		
	Diluted	NS	<0.05	NS	
Silicon	New				
	Untreated	<0.05			
	Concentrated	NS	NS		
	Diluted	NS	NS	NS	
Phosphorus	New				
	Untreated	NS			
	Concentrated	<0.05	NS		
	Diluted	NS	NS	NS	
Sulfur	New				
	Untreated	<0.05			
	Concentrated	NS	NS		
	Diluted	NS	NS	NS	

7.3.3.11 Defects following exposure for six months

There were no cracks observed in these samples. Cavities differed between treatments ($F_{3,37.1}$, P <0.0001). Convexities differed strongly between treatments (H = 40.3, d.f. = 3, P <0.0001). Smooth areas did not differ between treatments (H = 6.08, d.f. = 3, P = 0.108). There were marked differences between treatments for contaminants (H = 26.2, d.f. = 3, P <0.0001). The data are presented in Tables 7.38 and 7.39.

TABLE 7.38

Defects per unit area on the surface of PVC gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for six months. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks) for the abnormal distributions and the means and standard errors are shown for cavities (One Way ANOVA).

Defects	Treatment	n	Median	25%	75%
Contaminants	New	20	0	0	1
	Untreated	20	7	4	12
	Concentrated	20	5	4	6
	Diluted	20	2	0	6
Convexities	New	20	7	6	8
	Untreated	20	1	0	2
	Concentrated	20	1	1	3
	Diluted	20	2	1	4
Smooth*	New	20	0	0	0
	Untreated	20	0	0	0
	Concentrated	20	0	0	0
	Diluted	20	0	0	0
				Mean ± se	
Cavities	New	20		7.85 ± 0.406	
	Untreated	20		2.75 ± 0.410	
	Concentrated	20		2.4 ± 1.351	
	Diluted	20		3.3 ± 0.493	

* The mean for smooth = 0.025

TABLE 7.39

Comparison of the defects per unit area on the surface of PVC gloves following exposure to Top Clip Blue Shield® and weather for six months (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		**Treatments**			
		New	Untreated	Concentrated	Diluted
Cavities	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	NS	NS	
Contaminants	New				
	Untreated	<0.05			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	<0.05	
Convexities	New				
	Untreated	<0.05			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	<0.05	

7.3.3.12 *X-ray microanalysis following exposure for six months*

Carbon varied between treatments ($H = 8.70$, d.f. = 3, $P = 0.0336$). There were marked differences for oxygen ($F_{3,11} = 29.4$, $P < 0.0001$). Aluminium varied between treatments ($F_{3,11} = 3.92$, $P = 0.0397$). There were variations for silicon ($F_{3,11} = 16.8$, $P = 0.0002$). Phosphorus differed between treatments ($H = 13.8$, d.f. = 3, $P = 0.0032$). Sulfur differed strongly between treatments ($F_{3,11} = 82.7$, $P < 0.0001$). There were differences for chlorine ($F_{3,11} = 5.01$, $P = 0.0198$). A summary of the data is presented in Tables 7.40 and 7.41.

TABLE 7.40

Elements (counts per second) on the surface of PVC gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for six months. The medians, 25th and 75th percentiles are shown for the abnormal distributions (Kruskal-Wallis One Way ANOVA on Ranks). The means and standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Treatment	n	Median	25%	75%
Carbon	New	6	6600	6515	8744
	Untreated	3	10851	9395	14603
	Concentrated	3	10643	10571	12700
	Diluted	3	11993	11122	15766
Phosphorus	New	6	0	0	0
	Untreated	3	0	0	0
	Concentrated	3	154	71	219
	Diluted	3	0	0	0
				Mean ± se	
Oxygen	New	6	6264 ± 517		
	Untreated	3	13737 ± 1986		
	Concentrated	3	16157 ± 349		
	Diluted	3	17782 ± 1435		
Aluminium	New	6	549 ± 116		
	Untreated	3	1061 ± 107		
	Concentrated	3	1141 ± 107		
	Diluted	3	1321 ± 382		
Silicon	New	6	433 ± 72		
	Untreated	3	3705 ± 534		
	Concentrated	3	4340 ± 734		
	Diluted	3	4135 ± 944		
Sulfur	New	6	378 ± 23		
	Untreated	3	466 ± 59		
	Concentrated	3	1754 ± 140		
	Diluted	3	381 ± 84		
Chlorine	New	6	33321 ± 1731		
	Untreated	3	32574 ± 1518		
	Concentrated	3	39659 ± 668		
	Diluted	3	28311 ± 2518		

TABLE 7.41

Comparison of the elements per unit area on the surface of PVC gloves following exposure to Top Clip Blue Shield® and weather for six months (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or Dunn's method following One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		**Treatments**			
		New	Untreated	Concentrated	Diluted
Carbon	New				
	Untreated	NS			
	Concentrated	NS	NS		
	Diluted	NS	NS	NS	
Oxygen	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	NS	NS	
Aluminium	New				
	Untreated	NS			
	Concentrated	NS	NS		
	Diluted	<0.05	NS	NS	
Silicon	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	NS	NS	
Phosphorus	New				
	Untreated	NS			
	Concentrated	<0.05	<0.05		
	Diluted	NS	NS	<0.05	
Sulfur	New				
	Untreated	NS			
	Concentrated	<0.05	<0.05		
	Diluted	NS	NS	<0.05	
Chlorine	New				
	Untreated	NS			
	Concentrated	NS	NS		
	Diluted	NS	NS	<0.05	

7.3.3.13 Defects following exposure for seven months

Cracks differed between treatments (H = 9.60, d.f. = 3, P = 0.0223). Cavities differed between treatments, but the power of the tests was low ($F_{3,38.5}$, P <0.0001). Convexities varied markedly between treatments (H = 37.3, d.f. = 3, P <0.0001). There were differences between treatments for smooth areas (H = 12.5, d.f. = 3, P = 0.0059). There were strong differences between treatments for contaminants (H = 45.5, d.f. = 3, P <0.0001). The data are summarised in Tables 7.42 and 7.43.

TABLE 7.42

Defects per unit area on the surface of PVC gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for seven months. The medians, 25th and 75th percentiles are shown for the abnormal distributions (Kruskal-Wallis One Way ANOVA on Ranks). The means and standard errors are shown for the normal distributions (One Way ANOVA).

Defects	Treatment	n	Median	25%	75%
Contaminants	New	20	0	0	1
	Untreated	20	0	0	6
	Concentrated	20	7	5	8
	Diluted	20	0	0	0
Convexities	New	20	7	6	8
	Untreated	20	1	0	2
	Concentrated	20	0	0	3
	Diluted	20	4	2	5
Cracks	New	20	0	0	0
	Untreated	20	0	0	0
	Concentrated	20	0	0	0
	Diluted	20	0	0	1
Smooth*	New	20	0	0	0
	Untreated	20	0	0	0
	Concentrated	20	0	0	0
	Diluted	20	0	0	0
				Mean ± se	
Cavities	New	20		8 ± 0.4	
	Untreated	20		2 ± 0.3	
	Concentrated	20		4 ± 0.4	
	Diluted	20		5 ± 0.5	

* The mean for smooth = 0.05

TABLE 7.43

Comparison of the defects per unit area on the surface of PVC gloves following exposure to Top Clip Blue Shield® and weather for seven months. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		**Treatments**			
		New	Untreated	Concentrated	Diluted
Cavities	New				
	Untreated	<0.05			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	NS	
Contaminants	New				
	Untreated	NS			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	<0.05	
Convexities	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	<0.05	<0.05	
Cracks	New				
	Untreated	NS			
	Concentrated	NS	NS		
	Diluted	NS	NS	NS	
Smooth	New				
	Untreated	NS			
	Concentrated	NS	NS		
	Diluted	NS	NS	NS	

7.3.3.14 X-ray microanalysis following exposure for seven months

There were no differences for carbon concentrations between treatments ($F_{3,11}$ = 2.07, P = 0.1624). Oxygen varied powerfully between treatments ($F_{3,11}$ = 29.3, P <0.0001). Aluminium differed between treatments (H = 8.49, d.f. = 3, P = 0.0369) as did silicon (H = 10.1, d.f. = 3, P = 0.0178). There were variations for phosphorus (H = 13.8, d.f. = 3, P = 0.0032). There were strong differences for sulfur ($F_{3,11}$ = 23, P <0.0001). Chlorine differed between treatments ($F_{3,11}$ = 8.69, P = 0.0031). The data are presented in Tables 7.44 and 7.45.

TABLE 7.44

Elements (counts per second) on the surface of PVC gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for seven months. The medians, 25th and 75th percentiles are shown for the abnormal distributions (Kruskal-Wallis One Way ANOVA on Ranks). The means and standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Treatment	n	Median	25%	75%
Aluminium	New	6	424	387	624
	Untreated	3	3771	1864	4720
	Concentrated	3	193	126	493
	Diluted	3	375	363	386
Silicon	New	6	431	345	522
	Untreated	3	6085	3942	9874
	Concentrated	3	862	488	965
	Diluted	3	822	767	854
Phosphorus	New	6	0	0	0
	Untreated	3	0	0	0
	Concentrated	3	59	28	62
	Diluted	3	0	0	0
				Mean ± se	
Carbon	New	6	7577 ± 717		
	Untreated	3	9747 ± 1313		
	Concentrated	3	8770 ± 2335		
	Diluted	3	5222 ± 645		
Oxygen	New	6	6264 ± 517		
	Untreated	3	30933 ± 2449		
	Concentrated	3	18849 ± 4119		
	Diluted	3	14863 ± 1401		
Sulfur	New	6	378 ± 23		
	Untreated	3	449 ± 59		
	Concentrated	3	601 ± 23		
	Diluted	3	711 ± 20		
Chlorine	New	6	33321 ± 1731		
	Untreated	3	43941 ± 5573		
	Concentrated	3	29538 ± 8538		
	Diluted	3	59492 ± 2527		

TABLE 7.45

Comparison of the elements per unit area on the surface of PVC gloves following exposure to Top Clip Blue Shield® and weather for seven months (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or Dunn's method following One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		**Treatments**			
		New	Untreated	Concentrated	Diluted
Oxygen	New				
	Untreated	<0.05			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	NS	
Aluminium	New				
	Untreated	NS			
	Concentrated	NS	<0.05		
	Diluted	NS	NS	NS	
Silicon	New				
	Untreated	<0.05			
	Concentrated	NS	NS		
	Diluted	NS	NS	NS	
Phosphorus	New				
	Untreated	NS			
	Concentrated	<0.05	<0.05		
	Diluted	NS	NS	<0.05	
Sulfur	New				
	Untreated	NS			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	NS	
Chlorine	New				
	Untreated	NS			
	Concentrated	NS	NS		
	Diluted	<0.05	<0.05	<0.05	

7.3.4 Long-term exposures: nitrile-butadiene rubber gloves

Phosphorus was not detected on these samples.

7.3.4.1 Narrative account of visible and microscopic defects: nitrile-butadiene rubber

The Sol-Vex™ gloves became stiffer and paler in colour during the first month of exposure. The stiffness and discolouration increased over the months. The gloves had a tendency to buckle up, thus allowing small pools of water to accumulate. Quite a few insects and spiders died in these little water pools on the gloves exposed to the concentrated Top Clip Blue Shield® during this time. Spiders began to reside in the gloves after three months. An exposed glove is illustrated in Figure 7.4 showing embrittlement.

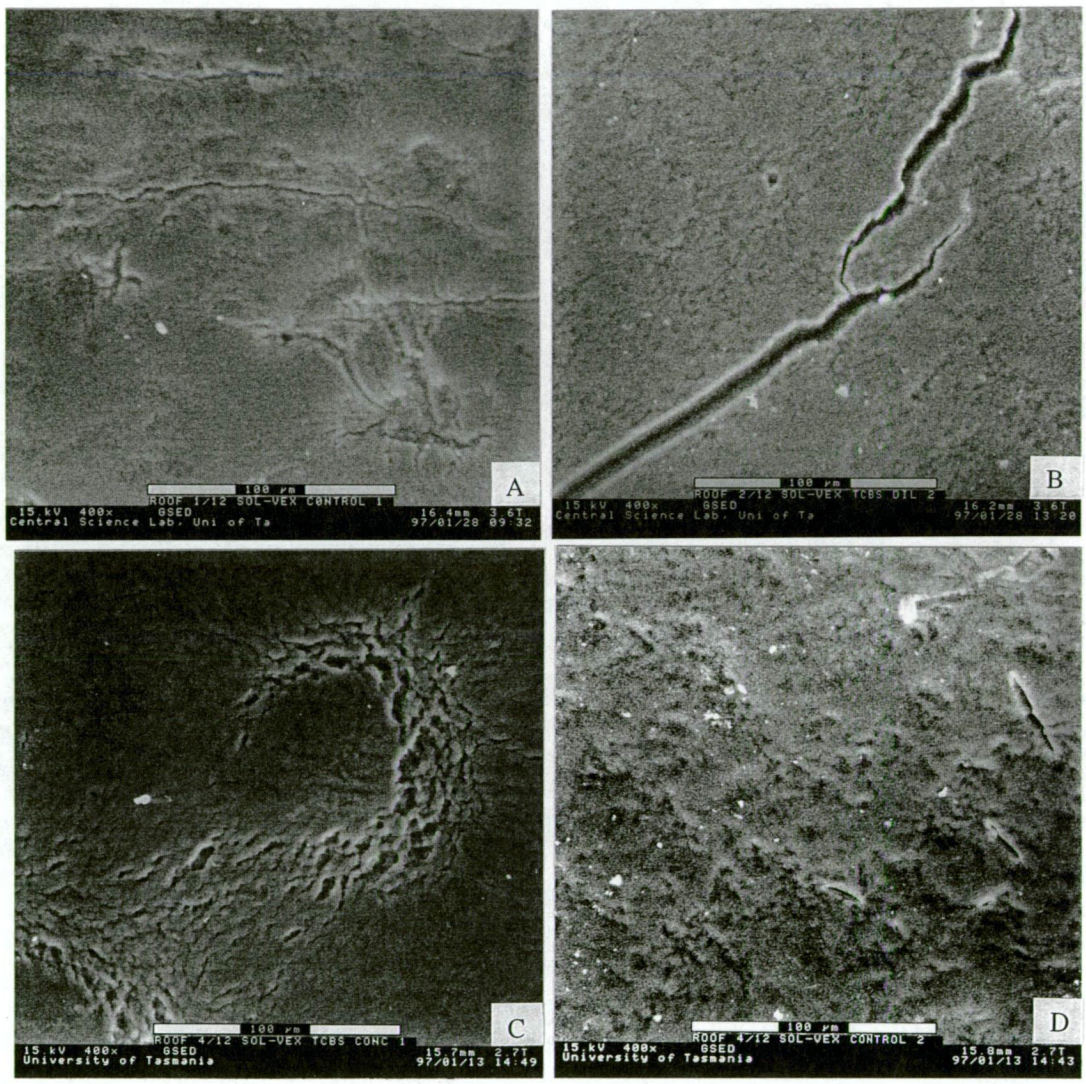
Microscopically at one month the surface topography was textured with some curved cracks in the untreated samples. One of the samples exposed to concentrated Top Clip Blue Shield® had wide linear cracks. At two months linear cracks were observed on the samples exposed to diluted Top Clip Blue Shield®, whereas the samples exposed to the concentrated Top Clip Blue Shield® had a combination of linear and curved cracks. The untreated samples had curved cracks only. Both types of cracks became more well defined, increased in length and size over the months. Many joined up at six months and by seven months the surface topography had an "Easter egg" like texture. A chronological illustration is given in Figure 7.5.

FIGURE 7.4

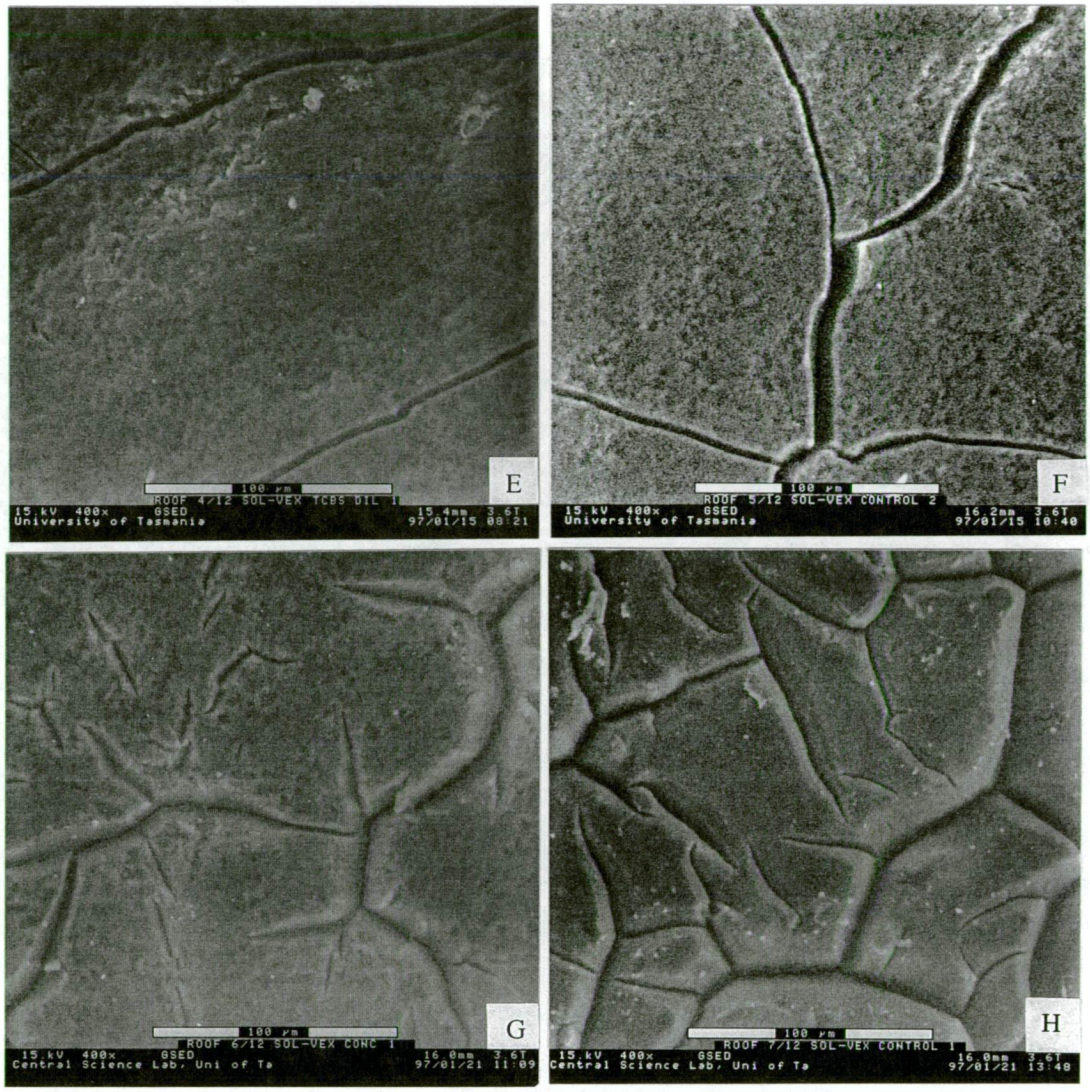
Embrittlement in Sol-Vex™ gloves following seven months outdoor exposure

FIGURE 7.5

Environmental scanning electron micrographs (400 x) detailing changes in Sol-Vex™ gloves following outdoor exposure



A: NBR following exposure for 1 month, showing fine curved cracks. B: NBR following exposure to diluted Top Clip Blue Shield® and weather for 2 months, showing linear cracks. C: NBR following exposure to concentrated Top Clip Blue Shield® and weather for 4 months, showing curved cracks. D: NBR following exposure to weather for 4 months, showing linear cracks and cavities.



E: NBR following exposure to diluted Top Clip Blue Shield® and weather for 4 months, showing linear cracks. F: NBR following exposure to weather for 5 months, showing brittle fractures. G: NBR following exposure to weather for 6 months, showing linear cracks. H: NBR following exposure to weather for 7 months, showing the typical "Easter egg" pattern.

7.3.4.2 Defects following exposure for one month

There were no slumps or smooth areas on the NBR samples for this exposure period. Cracks differed strongly between treatments ($H = 36.5$, d.f. = 3, $P < 0.0001$). There were marked differences for cavities between treatments ($H = 30.4$, d.f. = 3, $P < 0.0001$). Convexities differed strongly between treatments ($H = 36.1$, d.f. = 3, $P < 0.0001$). There were no differences for contaminants between treatments ($H = 7.68$, d.f. = 3, $P = 0.0531$). The data are summarised in Tables 7.46 and 7.47.

TABLE 7.46

Defects per unit area on the surface of NBR gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for one month. The medians, 25th and 75th percentiles are shown. (Kruskal-Wallis One Way ANOVA on Ranks.)

Defects	Treatment	n	Median	25%	75%
Cavities	New	20	7	5	9
	Untreated	20	3	3	5
	Concentrated	20	3	1	5
	Diluted	20	7	5	8
Contaminants	New	20	0	0	0
	Untreated	20	0	0	0
	Concentrated	20	0	0	5
	Diluted	20	0	0	0
Convexities	New	20	5	4	7
	Untreated	20	0	0	3
	Concentrated	20	0	0	0
	Diluted	20	4	2	5
Cracks	New	20	0	0	0
	Untreated	20	2	0	3
	Concentrated	20	1	0	2
	Diluted	20	0	0	0

TABLE 7.47

Comparison of the defects per unit area on the surface of NBR gloves following exposure to Top Clip Blue Shield® and weather for one month. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		**Treatments**			
		New	Untreated	Concentrated	Diluted
Cavities	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	NS	<0.05	<0.05	
Convexities	New				
	Untreated	<0.05			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	<0.05	
Cracks	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	NS	<0.05	<0.05	

7.3.4.3 X-ray microanalysis following exposure for one month

Carbon differed between treatments ($F_{3,11} = 3.77$, $P = 0.0439$), but this test was conducted below the desired level. There were variations for oxygen ($F_{3,11} = 316.9$, $P = 0.0002$). Aluminium varied strongly between treatments ($F_{3,11} = 49.3$, $P < 0.0001$), as did silicon ($F_{3,11} = 21.9$, $P < 0.0001$). Sulfur did not differ between treatments ($H = 3.86$, d.f. = 3, $P = 0.277$), nor did chlorine ($H = 5.86$, d.f. = 3, $P = 0.119$). A summary of the data is presented in Tables 7.48 and 7.49.

TABLE 7.48

Elements (counts per second) on the surface of NBR gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for one month. The medians, 25th and 75th percentiles are shown for the abnormal distributions (Kruskal-Wallis One Way ANOVA on Ranks). The means and standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Treatment	n	Median	25%	75%
Sulfur	New	6	1745	1683	3687
	Untreated	3	1638	1487	1697
	Concentrated	3	1721	1705	1901
	Diluted	3	1754	1750	1879
Chlorine	New	6	6420	6175	30219
	Untreated	3	5470	4965	6420
	Concentrated	3	5577	5193	5774
	Diluted	3	6003	5804	6111
				Mean ± se	
Carbon	New	6		6272 ± 790	
	Untreated	3		6633 ± 352	
	Concentrated	3		4943 ± 272	
	Diluted	3		3457 ± 241	
Oxygen	New	6		4882 ± 780	
	Untreated	3		10700 ± 546	
	Concentrated	3		10558 ± 563	
	Diluted	3		5893 ± 490	
Aluminium	New	6		404 ± 151	
	Untreated	3		168 ± 31	
	Concentrated	3		3260 ± 393	
	Diluted	3		93 ± 16	
Silicon	New	6		571 ± 137	
	Untreated	3		728 ± 297	
	Concentrated	3		2308 ± 135	
	Diluted	3		483 ± 30	

TABLE 7.49

Comparison of the elements per unit area on the surface of NBR gloves following exposure to Top Clip Blue Shield® and weather for one month (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or Dunn's method following One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		**Treatments**			
		New	Untreated	Concentrated	Diluted
Carbon	New				
	Untreated	NS			
	Concentrated	NS	NS		
	Diluted	NS	NS	NS	
Oxygen	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	NS	<0.05	<0.05	
Aluminium	New				
	Untreated	NS			
	Concentrated	<0.05	<0.05		
	Diluted	NS	NS	<0.05	
Silicon	New				
	Untreated	NS			
	Concentrated	<0.05	<0.05		
	Diluted	NS	NS	<0.05	

7.3.4.4 Defects following exposure for two months

There were no slumps or smooth areas on these samples. There were strong differences for cracks between treatments ($H = 22.7$, d.f. = 3, $P < 0.0001$). Cavities did not differ between treatments ($H = 2.33$, d.f. = 3, $P = 0.507$). There were no differences between treatments for convexities ($H = 5.48$, d.f. = 3, $P = 0.140$). Contaminants varied between treatments ($H = 10.1$, d.f. = 3, $P = 0.0176$). A summary of the data is given in Tables 7.50 and 7.51.

TABLE 7.50

Defects per unit area on the surface of NBR gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for two months. The medians, 25th and 75th percentiles are shown. (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatment	n	Median	25%	75%
Cavities	New	20	7	5	9
	Untreated	20	7	5	9
	Concentrated	20	8	6	9
	Diluted	20	8	7	9
Contaminants	New	20	0	0	0
	Untreated	20	0	0	0
	Concentrated	20	0	0	1
	Diluted	20	0	0	0
Convexities	New	20	5	4	7
	Untreated	20	4	2	5
	Concentrated	20	4	1	5
	Diluted	20	2	0	8
Cracks	New	20	0	0	0
	Untreated	20	2	0	3
	Concentrated	20	3	0	4
	Diluted	20	1	0	2

TABLE 7.51

Comparison of the defects per unit area on the surface of NBR gloves following exposure to Top Clip Blue Shield® and weather for two months. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		Treatments			
		New	Untreated	Concentrated	Diluted
Contaminants	New				
	Untreated	NS			
	Concentrated	NS	NS		
	Diluted	NS	NS	NS	
Cracks	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	NS	NS	

7.3.4.5 X-ray microanalysis following exposure for two months

Carbon varied between treatments ($F_{3,11} = 11.7$, $P = 0.0009$). There were strong variations for oxygen ($F_{3,11} = 55.3$, $P < 0001$). There were no differences for aluminium ($F_{3,11} = 0.842$, $P = 0.499$). Silicon varied between treatments ($F_{3,11} = 11.6$, $P = 0.0010$). Sulfur did not differ between treatments ($F_{3,11} = 0.340$, $P = 0.797$). Chlorine did not differ between treatments ($H = 5.86$, d.f. = 3, $P = 0.119$). A summary of the data is presented in Tables 7.52 and 7.53.

TABLE 7.52

Elements (counts per second) on the surface of NBR gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for two months. The medians, 25th and 75th percentiles are shown for the abnormal distributions (Kruskal-Wallis One Way ANOVA on Ranks). The means and standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Treatment	n	Median	25%	75%
Chlorine	New	6	6420	6175	30219
	Untreated	3	8152	5673	8163
	Concentrated	3	9961	9651	10221
	Diluted	3	7026	6020	7364
				Mean ± se	
Carbon	New	6		6272 ± 790	
	Untreated	3		7317 ± 1016	
	Concentrated	3		9691 ± 630	
	Diluted	3		12696 ± 437	
Oxygen	New	6		4882 ± 780	
	Untreated	3		12760 ± 1540	
	Concentrated	3		18218 ± 973	
	Diluted	3		19265 ± 239	
Aluminium	New	6		404 ± 151	
	Untreated	3		366 ± 116	
	Concentrated	3		669 ± 75	
	Diluted	3		401 ± 36	
Silicon	New	6		571 ± 137	
	Untreated	3		861 ± 128	
	Concentrated	3		1645 ± 92	
	Diluted	3		896 ± 63	
Sulfur	New	6		2416 ± 458	
	Untreated	3		1993 ± 310	
	Concentrated	3		2583 ± 46	
	Diluted	3		2521 ± 18	

TABLE 7.53

Comparison of the elements per unit area on the surface of NBR gloves following exposure to Top Clip Blue Shield® and weather for two months (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or Dunn's method following One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		**Treatments**			
		New	Untreated	Concentrated	Diluted
Carbon	New				
	Untreated	NS			
	Concentrated	<0.05	NS		
	Diluted	<0.05	<0.05	<0.05	
Oxygen	New				
	Untreated	<0.05			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	NS	
Silicon	New				
	Untreated	NS			
	Concentrated	<0.05	<0.05		
	Diluted	NS	NS	<0.05	

7.3.4.5 6 Defects following exposure for three months

There were no slumps or smooth areas on these samples. There were strong differences between treatments for cracks ($H = 57.1$, d.f. = 3, $P < 0.0001$). There were variations for cavities between treatments ($H = 11.1$, d.f. = 3, $P = 0.0110$). Convexities differed between treatments ($H = 12.6$, d.f. = 3, $P < 0.05$). Contaminants varied between treatments ($H = 17.5$, d.f. = 3, $P = 0.0006$). The data are presented in Tables 7.54 and 7.55.

TABLE 7.54

Defects per unit area on the surface of NBR gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for three months. The medians, 25th and 75th percentiles are shown. (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatment	n	Median	25%	75%
Cavities	New	20	7	5	9
	Untreated	20	5	4	10
	Concentrated	20	5	2	6
	Diluted	20	5	3	7
Contaminants	New	20	0	0	0
	Untreated	20	1	0	3
	Concentrated	20	0	0	0
	Diluted	20	0	0	0
Convexities	New	20	5	4	7
	Untreated	20	4	3	6
	Concentrated	20	2	0	5
	Diluted	20	2	0	5
Cracks	New	20	0	0	0
	Untreated	20	0	0	0
	Concentrated	20	3	2	4
	Diluted	20	1	1	2

TABLE 7.55

Comparison of the defects per unit area on the surface of NBR gloves following exposure to Top Clip Blue Shield® and weather for three months. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		**Treatments**			
		New	Untreated	Concentrated	Diluted
Cavities	New				
	Untreated	NS			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	<0.05	
Contaminants	New				
	Untreated	<0.05			
	Concentrated	NS	<0.05		
	Diluted	<0.05	<0.05	NS	
Convexities	New				
	Untreated	<0.05			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	NS	
Cracks	New				
	Untreated	NS			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	<0.05	

7.3.4.7 X-ray microanalysis following exposure for three months

Carbon varied between treatments ($F_{3,11} = 7.88$, $P = 0.0044$). There were variations for oxygen between treatments ($H = 10.8$, d.f. = 3, $P = 0.0131$). Aluminium did not vary between treatments ($F_{3,11} = 0.141$, $P = 0.9335$) nor did silicon ($F_{3,11} = 2.63$, $P = 0.1023$). There were no differences for sulfur ($H = 2.09$, d.f. = 3, $P = 0.554$). Chlorine did not differ between treatments ($H = 5.40$, d.f. = 3, $P = 0.145$). Tables 7.56 and 7.57 contain a summary of the data.

TABLE 7.56

Elements (counts per second) on the surface of NBR gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for three months. The medians, 25th and 75th percentiles are shown for the abnormal distributions (Kruskal-Wallis One Way ANOVA on Ranks). The means and standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Treatment	n	Median	25%	75%
Oxygen	New	6	3897	3772	7023
	Untreated	3	6452	5440	9126
	Concentrated	3	19129	18132	21651
	Diluted	3	20335	18584	20457
Sulfur	New	6	1745	1683	3687
	Untreated	3	2433	2033	2444
	Concentrated	3	2306	2218	4159
	Diluted	3	2450	2376	2513
Chlorine	New	6	6420	6175	30219
	Untreated	3	9352	9139	9558
	Concentrated	3	6020	2050	6539
	Diluted	3	8067	8041	8269
			Mean ± se		
Carbon	New	6	6272 ± 790		
	Untreated	3	5753 ± 2060		
	Concentrated	3	10513 ± 573		
	Diluted	3	12133 ± 515		
Aluminium	New	6	404 ± 151		
	Untreated	3	370 ± 73		
	Concentrated	3	498 ± 39		
	Diluted	3	397 ± 34		
Silicon	New	6	571 ± 137		
	Untreated	3	889 ± 116		
	Concentrated	3	1513 ± 549		
	Diluted	3	902 ± 63		

TABLE 7.57

Comparison of the elements per unit area on the surface of NBR gloves following exposure to Top Clip Blue Shield® and weather for three months (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or Dunn's method following One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		**Treatments**			
		New	Untreated	Concentrated	Diluted
Carbon	New				
	Untreated	NS			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	NS	
Oxygen	New				
	Untreated	NS			
	Concentrated	NS	NS		
	Diluted	<0.05	NS	NS	

7.3.4.8 Defects following exposure for four months

There were strong variations for cracks between treatments (H = 32.3, d.f. = 3, P <0.0001). Cavities differed between treatments (H = 9.54, d.f. = 3, P = 0.0230). There were no variations for convexities between treatments (H = 7.66, d.f. = 3, P = 0.0535). There were no differences for contaminants (H = 3.76, d.f. = 3, P = 0.288). The data are summarised in Tables 7.58 and 7.59.

TABLE 7.58

Defects per unit area on the surface of NBR gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for four months. The medians, 25th and 75th percentiles are shown. (Kruskal-Wallis One Way ANOVA on Ranks.)

Defects	Treatment	n	Median	25%	75%
Cavities	New	20	7	5	9
	Untreated	20	6	4	8
	Concentrated	20	4	3	6
	Diluted	20	7	4	10
Contaminants	New	20	0	0	0
	Untreated	20	6	0	10
	Concentrated	20	0	0	4
	Diluted	20	0	0	0
Convexities	New	20	5	4	7
	Untreated	20	5	2	7
	Concentrated	20	2	0	3
	Diluted	20	6	1	9
Cracks	New	20	0	0	0
	Untreated	20	0	0	0
	Concentrated	20	1	0	5
	Diluted	20	1	0	2

TABLE 7.59

Comparison of the defects per unit area on the surface of NBR gloves following exposure to Top Clip Blue Shield® and weather for four months. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		**Treatments**			
		New	Untreated	Concentrated	Diluted
Cavities	New				
	Untreated	NS			
	Concentrated	<0.05	<0.05		
	Diluted	NS	NS	<0.05	
Contaminants	New				
	Untreated	<0.05			
	Concentrated	<0.05	<0.05		
	Diluted	NS	<0.05	<0.05	
Convexities	New				
	Untreated	NS			
	Concentrated	<0.05	<0.05		
	Diluted	NS	NS	<0.05	
Cracks	New				
	Untreated	NS			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	NS	

7.3.4.9 X-ray microanalysis following exposure for four months

Carbon varied between treatments ($F_{3,11} = 14.5$, $P = 0.0004$). There were strong differences for oxygen between treatments ($F_{3,11} = 31.4$, $P < 0.0001$). There were no variations for aluminium ($F_{3,11} = 0.417$, $P = 0.745$). Silicon did not differ between treatments ($F_{3,11} = 1.53$, $P = 0.261$). There were no differences for sulfur ($F_{3,11} = 9.73$, $P = 0.440$). Chlorine did not differ between treatments ($H = 3.23$, d.f. = 3, $P = 0.358$). The data are presented in Tables 7.60 and 7.61.

TABLE 7.60

Elements (counts per second) on the surface of NBR gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for four months. The medians, 25th and 75th percentiles are shown (Kruskal-Wallis One Way ANOVA on Ranks). The means and standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Treatment	n	Median	25%	75%
Chlorine	New	6	6420	6175	30219
	Untreated	3	6676	5712	6904
	Concentrated	3	20744	19945	21319
	Diluted	3	6616	6613	6962
				Mean ± se	
Carbon	New	6		6272 ± 790	
	Untreated	3		16804 ± 1947	
	Concentrated	3		9282 ± 1085	
	Diluted	3		4703 ± 1940	
Oxygen	New	6		4882 ± 780	
	Untreated	3		32154 ± 4053	
	Concentrated	3		8361 ± 839	
	Diluted	3		8529 ± 3306	
Aluminium	New	6		404 ± 151	
	Untreated	3		442 ± 42	
	Concentrated	3		459 ± 60	
	Diluted	3		248 ± 61	
Silicon	New	6		571 ± 137	
	Untreated	3		803 ± 96	
	Concentrated	3		943 ± 135	
	Diluted	3		740 ± 19	
Sulfur	New	6		2416 ± 458	
	Untreated	3		2076 ± 148	
	Concentrated	3		2935 ± 108	
	Diluted	3		1935 ± 211	

TABLE 7.61

Comparison of the elements per unit area on the surface of NBR gloves following exposure to Top Clip Blue Shield® and weather for four months (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or Dunn's method following One Way ANOVA). Values are read at the junction, significance levels are determined at <0.05, NS = not significant.

Elements		**Treatments**			
		New	Untreated	Concentrated	Diluted
Carbon	New				
	Untreated	<0.05			
	Concentrated	NS	<0.05		
	Diluted	NS	<0.05	NS	
Oxygen	New				
	Untreated	<0.05			
	Concentrated	NS	<0.05		
	Diluted	NS	<0.05	NS	

7.3.4.10 Defects following exposure for five months

There were no slumps or smooth areas on these samples. Cracks differed strongly between treatments ($H = 32.3$, d.f. = 3, $P < 0.0001$). There were variations between treatments for cavities ($H = 9.54$, d.f. = 3, $P = 0.0230$). Convexities did not differ between treatments ($H = 7.66$, d.f. = 3, $P = 0.0535$). There were no differences between treatments for contaminants ($H = 3.76$, d.f. = 3, $P = 0.2883$). The data are shown in Tables 7.62 and 7.63.

TABLE 7.62

Defects per unit area on the surface of NBR gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for five months. The medians, 25th and 75th percentiles are shown. (Kruskal-Wallis One Way ANOVA on Ranks).

Defects	Treatment	n	Median	25%	75%
Cavities	New	20	7	5	9
	Untreated	20	9	7	11
	Concentrated	20	7	6	9
	Diluted	20	7	5	9
Contaminants*	New	20	0	0	0
	Untreated	20	0	0	0
	Concentrated	20	0	0	0
	Diluted	20	0	0	0
Convexities	New	20	5	4	7
	Untreated	20	4	1	10
	Concentrated	20	6	5	8
	Diluted	20	3	0	5
Cracks	New	20	0	0	0
	Untreated	20	1	0	2
	Concentrated	20	2	1	3
	Diluted	20	1	1	2

* The mean for contaminants = 0.04.

TABLE 7.63

Comparison of the defects per unit area on the surface of NBR gloves following exposure to Top Clip Blue Shield® and weather for five months. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		Treatments			
		New	Untreated	Concentrated	Diluted
Cavities	New				
	Untreated	<0.05			
	Concentrated	NS	<0.05		
	Diluted	NS	<0.05	NS	
Cracks	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	NS	NS	

7.3.4.11 X-ray microanalysis following exposure for five months

Carbon differed strongly between treatments ($F_{3,11} = 20.8$, $P < 0.0001$). There were very strong differences for oxygen between treatments ($F_{3,11} = 65.9$, $P < 0.0001$). There were no variations for aluminium ($F_{3,11} = 0.442$, $P = 0.7277$). Silicon differed between treatments ($F_{3,11} = 6.70$, $P = 0078$). Sulfur did not differ between treatments ($H = 3.83$, d.f. = 3, $P = 0.281$). There were no differences for chlorine ($H = 1.76$, d.f. = 3, $P = 0.624$). The data are summarised in Tables 7.64 and 7.65.

TABLE 7.64

Elements (counts per second) on the surface of NBR gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for five months. The medians, 25th and 75th percentiles are shown for the abnormal distributions (Kruskal-Wallis One Way ANOVA on Ranks). The means and standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Treatment	n	Median	25%	75%
Sulfur	New	6	1745	1683	3687
	Untreated	3	2252	2184	2272
	Concentrated	3	2508	2466	2573
	Diluted	3	2684	2651	2709
Chlorine	New	6	6420	6175	30219
	Untreated	3	8463	7907	8518
	Concentrated	3	9279	8456	9725
	Diluted	3	9284	8160	9431
				Mean ± se	
Carbon	New	6		6272 ± 790	
	Untreated	3		13323 ± 707	
	Concentrated	3		12117 ± 654	
	Diluted	3		1435 ± 1152	
Oxygen	New	6		4882 ± 780	
	Untreated	3		24075 ± 1241	
	Concentrated	3		24066 ± 1387	
	Diluted	3		24701 ± 2148	
Aluminium	New	6		404 ± 151	
	Untreated	3		348 ± 42	
	Concentrated	3		579 ± 87	
	Diluted	3		416 ± 53	
Silicon	New	6		571 ± 137	
	Untreated	3		813 ± 48	
	Concentrated	3		1350 ± 112	
	Diluted	3		943 ± 73	

TABLE 7.65

Comparison of the elements per unit area on the surface of NBR gloves following exposure to Top Clip Blue Shield® and weather for five months (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or Dunn's method following One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		**Treatments**			
		New	Untreated	Concentrated	Diluted
Carbon	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	NS	NS	
Oxygen	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	NS	NS	
Silicon	New				
	Untreated	NS			
	Concentrated	<0.05	NS		
	Diluted	NS	NS	NS	

7.3.4.12 Defects following exposure for six months

There were no smooth areas or slumps on these samples. Cracks differed strongly between treatments ($H = 34.7$, d.f. = 3, $P < 0.001$). There were differences for cavities between treatments ($H = 11$, d.f. = 3, $P = 0.0119$). There were marked differences for convexities between treatments ($H = 21$, d.f. = 3, $P = 0.0001$). Contaminants did not differ between treatments ($H = 2.01$, d.f. = 3, $P = 0.567$). The data are presented in Tables 7.66 and 7.67.

TABLE 7.66

Defects per unit area on the surface of NBR gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for six months. The medians, 25th and 75th percentiles are shown. (Kruskal-Wallis One Way ANOVA on Ranks.)

Defects	Treatment	n	Median	25%	75%
Cavities	New	20	7	5	9
	Untreated	20	4	1	7
	Concentrated	20	6	5	8
	Diluted	20	8	6	10
Contaminants*	New	20	0	0	0
	Untreated	20	0	0	0
	Concentrated	20	0	0	0
	Diluted	20	0	0	0
Convexities	New	20	5	4	7
	Untreated	20	0	0	4
	Concentrated	20	0	0	4
	Diluted	20	5	0	7
Cracks	New	20	0	0	0
	Untreated	20	2	1	5
	Concentrated	20	2	1	3
	Diluted	20	2	1	3

* The mean for contaminants = 0.09.

TABLE 7.67

Comparison of the defects per unit area on the surface of NBR gloves following exposure to Top Clip Blue Shield® and weather for six months. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		Treatments			
		New	Untreated	Concentrated	Diluted
Cavities	New				
	Untreated	<0.05			
	Concentrated	NS	<0.05		
	Diluted	NS	<0.05	NS	
Convexities	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	NS	<0.05	<0.05	
Cracks	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	NS	NS	

7.3.4.13 X-ray microanalysis following exposure for six months

There were no differences for carbon between treatments ($F_{3,11} = 3.01$, $P = 0.0765$). Oxygen differed very strongly between treatments ($F_{3,11} = 271.8$, $P < 0.0001$). Aluminium did not differ between treatments ($F_{3,11} = 0.284$, $P = 0.836$). Silicon varied between treatments ($F_{3,11} = 10.3$, $P = 0.0016$). There were no variations for sulfur ($H = 3.76$, d.f. = 3, $P = 0.289$) or for chlorine ($H = 3.16$, d.f. = 3, $P = 0.368$). The data are summarised in Tables 7.68 and 7.69.

TABLE 7.68

Elements (counts per second) on the surface of NBR gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for six months. (The medians, 25th and 75th percentiles are shown for the abnormal distributions (Kruskal-Wallis One Way ANOVA on Ranks). The means and standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Treatment	n	Median	25%	75%
Sulfur	New	6	1745	1683	3687
	Untreated	3	1864	1665	2014
	Concentrated	3	3054	2817	3062
	Diluted	3	2833	2832	3116
Chlorine	New	6	6420	6175	30219
	Untreated	3	17216	16870	17564
	Concentrated	3	9196	9006	9245
	Diluted	3	9033	8420	9737
			Mean ± se		
Carbon	New	6	6272 ± 790		
	Untreated	3	11106 ± 644		
	Concentrated	3	14573 ± 328		
	Diluted	3	12964 ± 5656		
Oxygen	New	6	4882 ± 780		
	Untreated	3	21440 ± 1091		
	Concentrated	3	29496 ± 576		
	Diluted	3	36803 ± 1020		
Aluminium	New	6	404 ± 151		
	Untreated	3	484 ± 87		
	Concentrated	3	572 ± 44		
	Diluted	3	482 ± 45		
Silicon	New	6	571 ± 137		
	Untreated	3	985 ± 57		
	Concentrated	3	1549 ± 132		
	Diluted	3	1087 ± 66		

TABLE 7.69

Comparison of the elements per unit area on the surface of NBR gloves following exposure to Top Clip Blue Shield® and weather for six months (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or Dunn's method following One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		**Treatments**			
		New	Untreated	Concentrated	Diluted
Oxygen	New				
	Untreated	<0.05			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	<0.05	
Silicon	New				
	Untreated	<0.05			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	NS	<0.05	

7.3.4.14 Defects following exposure for seven months

There were very strong differences for cracks between treatments ($H = 50.6$, d.f. = 3, $P < 0.0001$). Cavities also differed strongly ($H = 47.4$, d.f. = 3, $P < 0.0001$). There were strong variations for convexities ($H = 51.7$, d.f. = 3, $P < 0.0001$). Contaminants varied markedly between treatments ($H = 23$, d.f. = 3, $P < 0.0001$). There were no slumps or smooth areas on these samples. The data are presented in Tables 7.70 and 7.71.

TABLE 7.70

Defects per unit area on the surface of NBR gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for seven months. The medians, 25th and 75th percentiles are shown. (Kruskal-Wallis One Way ANOVA on Ranks.)

Defects	Treatment	n	Median	25%	75%
Cavities	New	20	7	5	9
	Untreated	20	3	3	4
	Concentrated	20	3	2	3
	Diluted	20	2	2	3
Contaminants	New	20	0	0	0
	Untreated	20	0	0	0
	Concentrated	20	1	0	8
	Diluted	20	0	0	1
Convexities	New	20	5	4	7
	Untreated	20	2	2	3
	Concentrated	20	2	0	4
	Diluted	20	0	0	0
Cracks	New	20	0	0	0
	Untreated	20	3	3	4
	Concentrated	20	3	2	3
	Diluted	20	2	2	3

TABLE 7.71

Comparison of the defects per unit area on the surface of NBR gloves following exposure to Top Clip Blue Shield® and weather for seven months. (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks.) Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Defects		**Treatments**			
		New	Untreated	Concentrated	Diluted
Cavities	New				
	Untreated	<0.05			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	NS	
Contaminants	New				
	Untreated	NS			
	Concentrated	<0.05	<0.05		
	Diluted	NS	NS	<0.05	
Convexities	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	<0.05	<0.05	
Cracks	New				
	Untreated	<0.05			
	Concentrated	<0.05	<0.05		
	Diluted	<0.05	<0.05	NS	

7.3.4.15 X-ray microanalysis following exposure for seven months

There were strong differences for carbon between treatments ($F_{3,11} = 36.9$, $P < 0.0001$). Oxygen varied between treatments ($H = 11.1$, d.f. = 3, $P = 0.0114$). Aluminium differed between treatments ($H = 9.30$, d.f. = 3, $P = 0.0256$). There were variations for silicon between treatments ($F_{3,11} = 9.13$, $P = 0.0025$). Sulfur did not vary ($H = 3.36$, d.f. = 3, $P = 0.3340$). Chlorine differed between treatments ($H = 11.4$, d.f. = 3, $P = 0.0099$). Tables 7.72 and 7.73 contain the summarised data.

TABLE 7.72

Elements (counts per second) on the surface of NBR gloves following exposure to the outdoor environment and concentrated or diluted Top Clip Blue Shield® for seven months. The medians, 25th and 75th percentiles are shown for the abnormal distributions (Kruskal-Wallis One Way ANOVA on Ranks). The means and standard errors are shown for the normal distributions (One Way ANOVA).

Elements	Treatment	n	Median	25%	75%
Oxygen	New	6	3897	3772	7023
	Untreated	3	39894	37928	44502
	Concentrated	3	33645	31049	36719
	Diluted	3	35245	28990	39568
Aluminium	New	6	206	151	782
	Untreated	3	935	906	955
	Concentrated	3	1129	1026	1227
	Diluted	3	661	641	701
Sulfur	New	6	1745	1683	3687
	Untreated	3	3207	3149	3233
	Concentrated	3	3432	3428	3587
	Diluted	3	3013	2968	3172
Chlorine	New	6	6420	6175	30219
	Untreated	3	1649	1542	2505
	Concentrated	3	2789	2512	3067
	Diluted	3	1890	1697	2057
				Mean ± se	
Carbon	New	6		6272 ± 790	
	Untreated	3		18195 ± 1300	
	Concentrated	3		15927 ± 73	
	Diluted	3		17075 ± 1502	
Silicon	New	6		571 ± 137	
	Untreated	3		1950 ± 182	
	Concentrated	3		1926 ± 483	
	Diluted	3		1469 ± 149	

TABLE 7.73

Comparison of the elements per unit area on the surface of NBR gloves following exposure to Top Clip Blue Shield® and weather for seven months (Student-Newman-Keuls method following Kruskal-Wallis One Way ANOVA on Ranks or Dunn's method following One Way ANOVA). Values are read at the junctions, significance levels are determined at <0.05, NS = not significant.

Elements		**Treatments**			
		New	Untreated	Concentrated	Diluted
Carbon	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	NS	NS	
Oxygen	New				
	Untreated	<0.05			
	Concentrated	NS	NS		
	Diluted	NS	NS	NS	
Aluminium	New				
	Untreated	NS			
	Concentrated	<0.05	NS		
	Diluted	NS	NS	NS	
Silicon	New				
	Untreated	<0.05			
	Concentrated	<0.05	NS		
	Diluted	<0.05	NS	NS	
Chlorine	New				
	Untreated	<0.05			
	Concentrated	NS	NS		
	Diluted	<0.05	NS	NS	

7.3.5 Liquid nitrogen immersion experiments

7.3.5.1 Liquid nitrogen immersion: polyvinyl chloride

The specimen that was fractured outside the liquid nitrogen was cracked in a linear fashion with well-defined edges (Figure 7.6). The specimen that was fractured inside the container of liquid nitrogen had visible fractures running at right angles from the main fracture line. The sample was taken from in between these visible fractures and was very smooth. Microscopically, there were no fractures and it was smooth (Figure 7.6).

7.3.5.2 Liquid nitrogen immersion: nitrile-butadiene rubber

The fracturing technique, either outside or submerged in liquid nitrogen, had very little effect on NBR. Both had cracks that were curved and the surface texture was uneven (Figure 7.7).

FIGURE 7.6

PVC gloves immersed in liquid nitrogen (400 x). A: fractured outside the container B: fractured inside the container

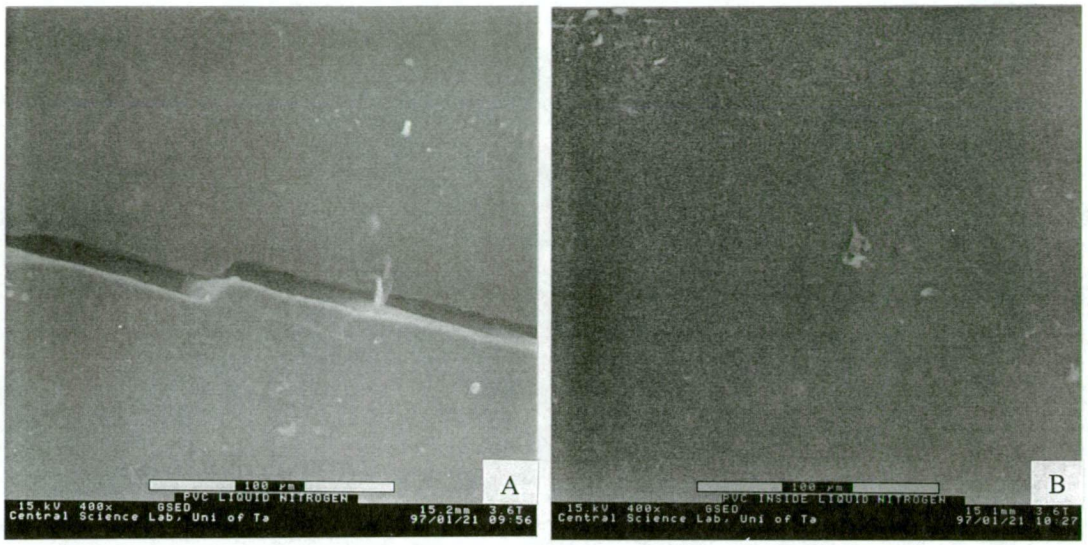
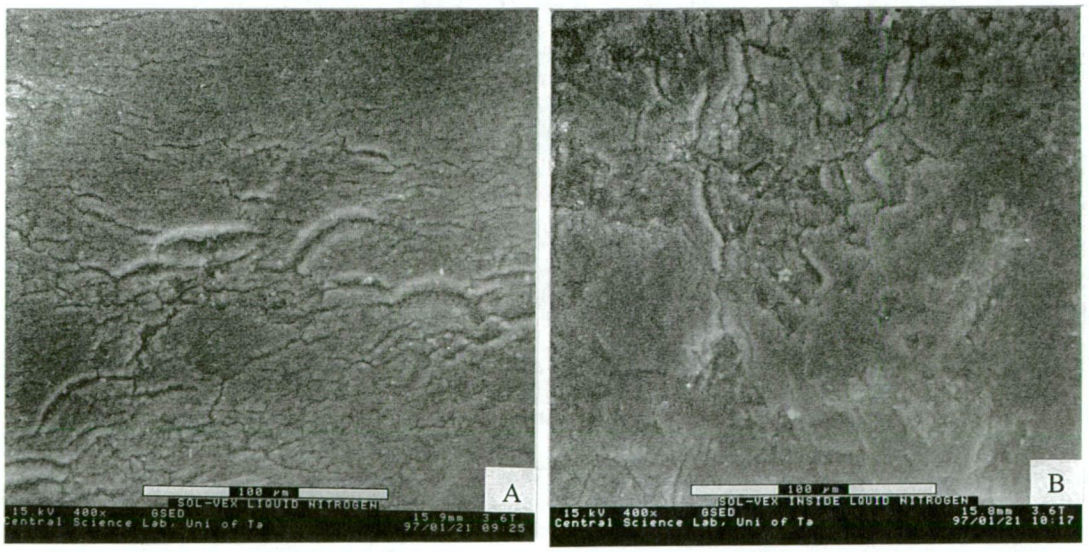


FIGURE 7.7

Sol-Vex™ gloves immersed in liquid nitrogen (400 x). A: fractured outside the container B: fractured inside the container



7.4 Discussion

The short-term exposure studies are discussed first, followed by the long-term exposure studies. The interpretation of the liquid nitrogen immersion experiments is integrated with the physical defects in the long-term exposure studies.

7.4.1 Short-term exposure experiments

The short-term exposure results illustrate the nature of the initial attack by formulated OPs on two widely used CPGs. The surface layer of the gloves was impacted in various ways suggestive of chemical degradation. The short exposure times and the newness of the tested gloves increase the likelihood that the observed defects are the result of chemical attack and not dissociation of polymers caused by aging, weathering, use patterns or other impacts.

7.4.1.1 Polyvinyl chloride gloves

There was no clear trend for cavities on the PVC gloves during the short-term exposures. The combination of environmental conditions and concentrated Top Clip Blue Shield® caused cavities on the 6/4/95, but not on the 28/4/95. Under identical environmental conditions the diluted Malathion® caused cavities on the 10/5/95, in contrast to the Lorsban® which did not. These contrasting results are most likely indicative of the inferior quality of these gloves and their irregular surface texture.

The results for convexities were ambiguous and it can be assumed that they were part of the manufacturing process, as established in Chapter Five (5.4.1). Lorsban® and sunlight exposure did not cause convexities on the PVC gloves. On the same day, there were more convexities on the untreated samples in the Malathion® experiment. Top Clip Blue Shield® had variable results. On the 6/4/95, the exposed untreated sample was similar to the sample treated with dilute Top Clip Blue Shield®, but the covered control was the same as the exposed untreated sample on the 6/4/95 and the sample treated with the concentrated Top Clip Blue Shield® on the 28/4/95.

Polyvinyl chloride exposed to sunlight and OPs is quite resistant to cracking. Cracks were not a significant defect for the short-term exposures.

Smooth areas were not a result of short-term exposure to sunlight and OPs.

7.4.1.2 Nitrile-butadiene rubber gloves

The results for cavities in the Sol-Vex™ gloves for the short-term exposure experiments were distinctive. Some cavities were caused by diluted Top Clip Blue Shield®, concentrated Lorsban® and concentrated Malathion®. Sunlight and

temperature had no influence on the number of cavities in the short-term exposure studies as there were no significant differences between the untreated covered and exposed samples. Malathion® was less aggressive than Lorsban® on these gloves.

Convexities were more evident on the treated samples, indicating that the OP exposure had an impact. It is conceivable that there was some absorption of the water and/or OPs that gave rise to swelling in some areas. Temperature and UV radiation were not responsible for causing convexities as there were no significant differences between the untreated covered and exposed samples.

There were few contaminants on the Sol-Vex™ gloves and most were confined to the treated gloves. Sol-Vex™ gloves are not tacky as the PVC gloves are, and therefore contaminants would not adhere as readily. This may also indicate that the washing technique was effective for Sol-Vex™ in the removal of contaminants.

The incidence of cracking overall is small, but of major concern because it may be a precursor to penetration. Cracking is higher with the Sol-Vex™ gloves and occurred over three challenges in the short-term exposure studies. The diluted Lorsban® and Malathion® contributed to cracking and this may be related to the volatility of these OPs. Cracking may be related to water absorption leading to swollen convexities that contract during the drying out process and thus lead to crack formation, as discussed in Chapter Five (5.4.1), (Engel *et al.* 1981, p.177). Top Clip Blue Shield® did not have this effect, and this may be due to its greater viscosity which would slow its evaporation time and therefore lower the risk of cracking. Sunlight did cause cracking on the 28/4/95 on the untreated exposed sample and this may be related to the higher UV-B reading. The temperature alone was not responsible for the cracking as there were none on the covered control. It may be possible that the higher temperature may have caused expansion of the specimen and/or it may have cracked when stored in the refrigerator at the cooler temperature, although this is unlikely as the covered control had no cracks. However, the surface temperature of the exposed glove would have been greater than the covered control due to heat absorption when outside.

Slumps were a feature of the new Sol-Vex™ gloves and although there were differences between the groups on several of the experiments these can only be related to the manufacturing process, rather than to any of the exposures. There were no slumps on the new samples for the long-term exposure experiments. Therefore, this defect is specific to that particular batch used in the short-term exposure experiments.

Smooth areas were not a product of short or long-term outdoor and OP exposure.

7.4.2 Long-term exposure experiments

The long-term exposure results describe the degradation processes. It is highly probable that these processes include oxidation, photo-oxidation, hydrolysis and weathering (Chapter Three, 3.4).

7.4.2.1 Polyvinyl chloride gloves

There were tactile changes felt in these gloves after four months outdoor exposure, since they became sticky to touch. After five months there were noticeable macroscopic structural changes. There were distinctive circumscribed areas that had an intensely uneven surface topography, with raised mounds and a very degraded appearance. These areas had noticeable colour changes, which is an indication of aging (Chapter Three, 3.4.1). It is probable that this restructuring was associated with plasticiser migration and a redistribution of the elements.

An interpretation of the microscopic defects follows.

7.4.2.1.1 *Defects in polyvinyl chloride gloves*

Slumps were not a feature of polyvinyl chloride, as identified in Chapter Five (5.3).

There was a loss of cavities associated with long-term exposure. It is possible that some of the cavities may have been filled in or occluded by particulate matter. There were major structural changes observed on PVC over time. Throughout the months of exposure some cavities had well-defined perimeters, whereas others were less distinctive and were more like depressions with blurred perimeters. Those with distinctive perimeters were most likely cavities that were associated with the manufacturing processes. Those with the blurred perimeters were most probably associated with weathering and structural changes. Some of the smaller cavities were found on samples that had an etched appearance and this is most probably due to chemical attack, *e.g.* oxidation (Figure 7.3). Cavities were not sub-classified according to these differences and this may be continued in future research.

Convexities decrease with long-term exposure to sunlight. Convexities were even less evident at five, six and seven months exposure. This is related to the structural changes that occurred as a result of degradation. Typically, there were fewer on the untreated samples, and this may be because the Top Clip Blue Shield® permeated into the PVC, and, as this permeation reached a state of equilibrium, no more convexities were formed. After the equilibrium state had been reached convexities were eroded by natural weathering. Another possibility is that the covering layer of Top Clip Blue

Shield® prevented some erosion of the convexities in the earlier months and as the pesticide concentration diminished erosion occurred.

There was a general trend for contaminants to be a feature of the treated samples. This was an expected outcome related to particulate fallout from the atmosphere and the surface tackiness of the PVC gloves. (This tackiness is a notable feature of fresh PVC gloves, in particular.)

Cracks were not observed until after four months exposure. These cracks were very fine and were observed on those samples that had an overall etched appearance suggestive of chemical degradation, such as oxidation, photo-oxidation and/or hydrolysis. It was not clear if the larger linear cracks that developed at six and seven months were propagated from the finer cracks that were observed first (Figure 7.3).

Cracking was observed in the liquid nitrogen experiments. The fist smashing technique produced microscopic brittle fractures whereas the plier snapping technique did not (Figure 7.6). The difference is due to the real forces applied to the material. The fist smashing technique applied a force to the whole specimen, which resulted in microscopic linear fractures. The PVC began to thaw very quickly when removed from the liquid nitrogen and this may have influenced the fracture pattern. The plier snapping technique applied a more concentrated force to the centre of the specimen, which resulted in a cleaner fracture line with visible smaller fractures occurring at right angles to it and no microscopic fractures.

The similarities between the exposed and immersed PVC suggest that embrittlement was a feature of the exposed PVC after six months.

In the long-term exposure experiments, smooth areas were not a statistical reportable variable until after six and seven months exposure. This is due to the highly uneven nature of the surface structure at this time, caused by degradation.

7.4.2.1.2 *Chemical changes that occurred in polyvinyl chloride gloves during long-term exposure*

Carbon concentrations in PVC were not affected by long-term exposure to sunlight and/or Top Clip Blue Shield®. Oxygen increased with long-term exposure, suggesting that oxidation was a major reaction. Generally, there were smaller concentrations on the new samples, and this suggests that the increased oxygen was probably related to chemical reactions of the surface of PVC and environmental agents.

Aluminium was detected in higher concentrations on the untreated samples in most cases. Aluminium became a significant variable after four months, with the exception of the two month treatments. Aluminium is probably related to dirts and other contaminants, as previously suggested. After five months exposure, the PVC was sticky to touch and therefore adhesion of dirts and dusts would have been relatively easy.

Silicon presented a similar profile to aluminium, having lesser concentrations on the new samples. Silicon was most probably associated with contaminants. The fluctuation of silicon and aluminium concentrations is most likely related to the weather, *e.g.* wind and rain cleansing the gloves.

Phosphorus from concentrated Top Clip Blue Shield® was detected right through to seven months exposure. The concentrations were only in small amounts, nevertheless it was an unexpected result as it was anticipated that Top Clip Blue Shield® would have volatilised, eroded or washed off. This is an interesting and important finding, because, if phosphorus can be retained for such a long time period, it begs the question as to what happens with repeated exposures.

Typically, sulfur concentrations were higher on the treated samples. There were some anomalies in this data set. There were higher concentrations on the samples exposed to concentrated and diluted Top Clip Blue Shield® for the four month exposure. Also, there were higher concentrations for the untreated sample at five months and for the sample treated with Top Clip Blue Shield® at six months. Some of the sulfur has been retained from the Top Clip Blue Shield® treatment and the remainder has come from environmental sources.

Long-term exposure to Top Clip Blue Shield® and sunlight did not influence chlorine concentrations in PVC. Chlorine became significant at six and seven months but there was no trend evident, with highest level on the sample treated with concentrated Top Clip Blue Shield® and lowest on the sample treated with dilute Top Clip Blue Shield®. The opposite results were obtained for the seven month exposure period. These unusual results may be associated with the redistribution of chlorine associated with the degradation process.

7.4.2.2 Nitrile-butadiene rubber gloves

Discolouration and stiffness were noticeable visual and tactile changes that occurred in the Sol-Vex™ gloves after exposure for one month. It seems likely that the stiffness

and discolouration were associated with a loss or migration of UV stabilisers and/or antiozonants and other aging processes, which is part of weathering.

The microscopic defects are discussed next.

7.4.2.2.1 *Defects in nitrile-butadiene rubber gloves*
Smooth areas were not a significant characteristic of the NBR experiments.

Cavities were a predominant defect in the new gloves for five months. It is therefore apparent that the number of cavities decreased with exposure, a similar finding to PVC. This trend does not continue through to seven months, and it is likely that the processes of embrittlement and degradation gave rise to cavities. Cavities on the new Sol-Vex™ gloves were less well defined, having irregular perimeters, than PVC. Generally the pattern and characteristics of these cavities did not change over time.

The number of convexities decreased with exposure. This is similar to the PVC results, although Sol-Vex™ gloves had fewer convexities on the treated samples. This suggests that Sol-Vex™ gloves are more resistant to permeation by Top Clip Blue Shield® than PVC. It also corroborates the PVC finding that convexities are subject to erosive forces over time.

There were fewer contaminants on these gloves than on the PVC, because they are not as tacky and therefore adhesion of particulates is more difficult. After four months exposure, contaminants became insignificant and this is probably related to embrittlement where the gloves became more rigid and contaminants would have washed off more easily.

Long-term exposure to weather and OPs caused cracking in Sol-Vex™ gloves. There were two types of crack formations observed in these studies; small curved and large linear. Both types of cracks coexisted, and both were observed after one month exposure and thereafter. It seems likely that the curved cracks were related to ozone attack. It is feasible to assume that antiozonants, which normally diffuse through to the surface of the material, dissipated, thus leaving the NBR vulnerable to ozone attack (Chapter Three, 3.3.2.2.1). The linear cracks are more likely to be associated with embrittlement. As the NBR became more brittle linear cracks occurred more frequently and eventually joined to give the "Easter egg" pattern. This is similar to the patterns described by Engel (1981, p.177).

The two freeze fracturing techniques did not produce different results (Figure 7.7), as was the case with PVC. This is probably because the Sol-Vex™ gloves were not lined and therefore freezing may have been more uniform, and consequently thawing may not have occurred as quickly as with PVC. This technique was unable to replicate embrittlement in NBR.

7.4.2.2.2 *Chemical changes that occurred in long-term exposure of nitrile-butadiene rubber gloves*

Carbon concentrations varied during the long-term exposures, although no trend was evident. The increased oxygen concentrations on the exposed samples were related to weathering where the chemical attack was caused by oxygen.

Aluminium and silicon concentrations were related to contaminants. The increased concentrations of both at seven months on the samples exposed to concentrated Top Clip Blue Shield® correlate with the data for contaminants. The sample taken after seven months exposure was rather dirty.

The surface of NBR did not retain any Top Clip Blue Shield® residues. Sulfur concentrations, which are part of the manufacturing process (Chapter Three, 3.6.2), were not affected by the long-term exposures and no phosphorus was detected.

Chlorine was not a significant variable until concentrations decreased at seven months. This is most likely related to the heavier loading of contaminants obscuring the chlorine.

7.5 Chapter Summary And Conclusions

The short-term exposure studies were conducted on days that were suited to pesticide application. Cavities and convexities were the predominant defects during these short-term exposure studies. Convexities and cavities were more difficult to evaluate for the PVC samples because many are also produced during manufacture. The PVC gloves were fairly resistant to cracking, whereas Sol-Vex™ did crack. Smooth areas were not a feature for both types of gloves. The PVC gloves performed slightly better than the Sol-Vex™ in spite of their inferior quality. These experiments can only relate to a farm worker donning a new pair of gloves, working for only four hours and spilling or splashing the glove with an OP. Nevertheless this method provides a good guide for initial exposure effects.

The long-term exposure studies provide a valuable insight into the degradation processes that occur over time. It seems highly probable that degradation in PVC is

associated with plasticiser migration and the redistribution of elements. This in turn leads to dramatic structural changes.

Discolouration was an indicator for aging in both types of gloves. This phenomenon occurred much more slowly in the PVC gloves, which is undoubtedly related to the thickness (Chapter Three, 3.7.2.2). (The PVC gloves were much thicker than the Sol-Vex™ gloves.) Both types of exposed gloves consistently had higher concentrations of oxygen, suggesting that oxidation was the main chemical process that occurred, which is probably associated with the UV load.

Degradation in the Sol-Vex™ gloves was much more rapid. The early signs of weathering and aging were discolouration and embrittlement, which in turn led to the extensive cracking. It therefore seems that if farmers are to use these gloves they should be replaced very frequently and discarded before discolouration occurs.

The liquid nitrogen experiments were able to induce embrittlement in PVC but not in Sol-Vex™. These techniques could be developed further in an attempt to replicate working conditions.

In conclusion, it is apparent that Sol-Vex™ gloves have superior chemical resistance properties to PVC gloves. However, they are unable to withstand outdoor conditions as well. Therefore, the PVC gloves should be the preferred choice for farmers.

Chapter Eight

Conclusions And Recommendations

8.1 Introduction

People who work with pesticides make up the largest occupational risk group, many of whom are farmers. In Tasmania, farms are generally small scale agricultural enterprises and typically one person is responsible for the mixing, loading and application of pesticides. Hands are the principal anatomical site contaminated during pesticide application and CPGs should provide a substantial barrier between hands and pesticides.

Farmers have unique requirements for CPGs, which must have effective chemical resistance properties, be robust enough to withstand the outdoor environment, be strong enough to withstand heavy work, have good grip functionality, allow for fine motor coordination and be comfortable to wear. Factors that influence glove integrity include manufacturing processes, glove thickness, their care, weather conditions and pesticide/solvent /polymer interactions.

Permeation studies dominate the technical literature. Permeation of solvents through CPGs has constituted a major part of all the permeation studies. Nelson *et al.* (1981) provided a modern foundation with their experiments describing permeation behaviour (Figure 3.2). Studies of pesticide permeation followed and Schwope *et al.* (1992) found that carrier solvents permeated at a greater rate than the active ingredients. Many pesticide formulations contain a variety of carrier solvents. Farmers use their CPGs for a variety of pesticide applications, thus demonstrating that most of the permeation testing is not applicable to real-life agricultural situations.

Other testing procedures have been discussed. Penetration testing is much simpler than permeation testing and involves air and water leak tests. Degradation testing involves measurements of weight gain or loss, elongation, thickness and tensile strength.

8.2 Identification Of Defects

This research has applied several experimental methods that have examined the efficacies of CPGs worn by farmers, with a focus on the surface topography. This process has involved the marriage of several scientific disciplines such as pesticide science, material science, microscopy, occupational hygiene and climatology.

This thesis has supported my original hypothesis:

> That due to poor quality control, no protocols in glove care and patchy promotion of their usage, I predict that chemically protective gloves are inadequate for farmers needs.

Invaluable information has been gained about the types of CPGs farmers are using. This is the first study of its kind, since prior to this study all knowledge was anecdotal. Red PVC gloves, made in China, dominate the market. These gloves are of inferior quality containing many inclusions, indicative of a lack of quality control procedures. Microscopically, there were significant differences between different batches of the new PVC gloves, which also points to poor quality control procedures. Slumps were an indicator of differing quality control measures on the new Sol-Vex™ gloves, but these cannot be regarded as serious flaws in the material.

Nitrile-butadiene rubber gloves were the second most common type collected. These gloves all came from the same source, Tahune Fields, an organisation that had a policy for using a double-gloving technique. Both types of NBR gloves, Sol-Vex™ and MSA™, were of superior and more uniform quality than the PVC.

The other types of gloves collected were not promoted as CPGs. Two types of NR gloves were collected, washing-up gloves and Hy-Care™, both made by Ansell Edmont. These gloves are designed for cleaning purposes and not for chemical resistance. Other gloves collected included, thin unidentified PVC, leather and cotton/leather, all of which are extremely unsuitable for pesticide application. Farmers need more information about the suitability of gloves for pesticide application at the point of sale and on the pesticide container labels.

Generally, the condition of the collected gloves was poor, fewer than half of them being intact. The visible failures included cracks, splits, macropores, punctures and abrasions. These types of failures will allow or enhance penetration and/or permeation of pesticide formulations and thus increase the risk of dermal exposure to farmers. It was therefore concluded that farmers need to be encouraged to check their gloves regularly and certainly before use.

The gloves from the exchange program had a mean age of two years. The relatively high level of visible failures in these gloves indicates that CPGs should not be used for more than one pesticide application season.

Farmers tend to treat their gloves in a haphazard manner and unfortunately the maintenance factors were confounded and therefore no conclusions could be drawn. Storage and cleaning methods for CPGs are areas that require much more research.

The comfort, fit and durability were of interest to those farmers who used the Hy-Care™ and Solvgard™ gloves, which are contoured to fit a hand form. The NBR gloves were also contoured, but their lack of durability for farm work was a criticism made of them. Polyvinyl chloride gloves leave a residual odour on the skin, although this could be lessened by wearing thin gloves underneath, improving the lining or adding a non-toxic deodoriser. If thin gloves are to be worn underneath PVC gloves they should be a type of CPG because if, for example, cotton gloves were to be used they may act as a reservoir for pesticides once contaminated.

8.3 Classification Of Defects

The development of a taxonomy of the surface physical defect in CPGs has been proven to be an effective comparative tool for new and exposed gloves. The gridded template proved to be a satisfactory and reliable tool for methodically counting the defects. The main defects identified were cavities, convexities, cracks, crazes, slumps, smooth areas and contaminants. This classification system could be used by glove manufacturers to check the quality of their gloves.

Cavities can be a precursor for early failure of gloves. These depressions can harbour pesticides and other contaminants and along with the decreased thickness in these areas permeation and/or penetration may be enhanced. Cavities were the predominant type of defects found on PVC gloves and included new gloves, thus indicating poor quality control measures. Cavities were also formed in response to chemical attack and working conditions. There were no significant findings for cavities following the short-term exposures to three OPs and sunlight. Long-term exposure to weather and OPs leads to a decrease in the number of cavities, possibly because these cavities are filled in as a result of the redistribution of the elements as embrittlement progresses.

Cavities were a product of the manufacturing processes on the MSA™ gloves but not the Sol-Vex™. Sol-Vex™ gloves sometimes responded to chemical challenges with the formation of cavities but on a lesser scale than PVC gloves. Some cavities on Sol-Vex™ gloves were caused by short-term exposure to sunlight and diluted Top Clip Blue Shield® and concentrated Lorsban®. Cavities were not consequential from long-term outdoor exposure.

While some convexities were due to the manufacturing processes, particularly in the more textured gloves, others were a result of chemical attack and the initial solvation causing swelling of the polymer, or convexities.

Convexities in new PVC gloves were extremely variable, suggesting poor quality control measures. These defects were related to the manufacturing processes in the more textured NR, MSA™ and PVC/NBR gloves. Convexities may enhance grip function in these more textured gloves.

The variability in PVC gloves led to insignificant differences in defects resulting from the short-term exposures to three different OPs and sunlight. Following the short-term exposures to sunlight and OPs some convexities were found on the treated Sol-Vex™ gloves, suggesting that permeation had occurred. These defects were eroded with use and long-term exposure in both PVC and Sol-Vex™ gloves.

Smooth areas were mainly confined to the PVC gloves. This phenomenon was found on the new gloves and those immersed in some of the OPs. They were also found on the gloves that had been subjected to long-term outdoor exposures after six months. The smooth areas on the new gloves indicate the non-uniform quality of these gloves. After chemical exposure, smooth areas may be related to the convexities, *e.g.* a plateau region on a convexity that occurred as the result of permeation. In the long-term exposure experiments, these smooth areas were related to the extremely uneven surface, which is a product of degradation.

Crazes were uniquely a feature of the used Sol-Vex™ gloves. Crazing cannot be regarded as a true material failure as it does not have any effect on the strength of the polymer. Because crazing was not a feature of the long-term exposure experiments, it indicates that it was due to the cleaning or storage procedures at Tahune Fields. Washing in detergent and water is the most likely explanation. Crazing can act as a precursor to cracking and therefore cleaning procedures for each type of CPG requires much more research.

Cracking can be classified as a critical defect because cracks will continue to propagate and penetration can readily occur. Essentially two types of cracks were observed—smaller curved cracks that were related to chemical attack, and larger linear cracks that were associated with embrittlement. Generally the PVC gloves were more resistant to chemically induced cracking.

Cracks were associated with working conditions in PVC and NBR gloves. Cracking occurred in PVC gloves following exposure to Top Clip Blue Shield® after thirty-six hours immersion. Cracks were also a feature of some of the Sol-Vex™ gloves in the immersion experiments. It is likely that permeation of the pesticide formulation occurred, which resulted in swelling, and then, during the drying out process, contraction occurred and gave rise to cracking.

Polyvinyl chloride gloves were resistant to cracking during the short-term exposure experiments, unlike Sol-Vex™ gloves, which did crack in three of these experiments. Some of these cracks were associated with sunlight, Lorsban® and Malathion® exposures. However, cracking also occurred on the untreated sample on the day with the highest UV-B reading. This demonstrated the unsuitability of these gloves for outdoor work even for short periods.

Cracking that occurred as a result of the long-term exposures is related to embrittlement in PVC gloves. Two different patterns of cracks were noted on the Sol-Vex™ gloves in the long-term exposure experiments—smaller curved cracks, which were probably associated with ozone attack, and linear cracks that eventually joined up to resemble an "Easter egg" pattern, which was representative of embrittlement. Embrittlement was replicated for PVC, but not for Sol-Vex™, in the laboratory liquid nitrogen immersion experiments. Generally, PVC gloves were more resistant to cracking and therefore more suited to outdoor work.

8.4 Chemical Analyses

Energy-dispersive spectroscopy has proven to be an effective method for comparative elemental analysis on CPGs. This is the first time that this method has been used on CPGs and has provided unique information about their constituents. This information has been considered proprietary and is not available in the public domain. The significant peaks identified for CPGs were carbon, oxygen, aluminium, silicon and chlorine.

Carbon was a constituent of all CPGs, as expected. Generally,the concentration of carbon decreased with normal agricultural working conditions. It is evident that this trend was associated with contaminants, pesticides and other materials that obscured the surface and therefore the detector could not analyse the concentration of the element effectively. This masking effect was not as noticeable on the CPGs in the long-term exposure experiments.

Oxygen was an integral component of all the CPGs. Generally, oxygen concentrations decreased after use on the PVC and MSA™ gloves. This may have been due the masking effect already noted and/or their composition. The Sol-Vex™, Hy-Care™ and washing-up gloves generally exhibited an increase in oxygen concentrations following use. These higher concentrations were probably due to chemical reactions such as oxidation, photo-oxidation, hydrolysis and/or the presence of contaminants.

Oxygen was also a component of the pesticide formulations as shown by the results of the one minute immersion experiments. The higher concentrations detected on the immersed samples may also indicate that some reactions had occurred. The results from the other immersion experiments suggest that the permeation process occurred at different rates for different pesticides, and that oxygen levels initially increased followed by a decline.

Typically, oxygen concentrations increased with long-term exposure on PVC and Sol-Vex™ gloves, and was accompanied by degradation. In the first two months there were no visible signs of degradation of PVC gloves, but Sol-Vex™ gloves had already begun to stiffen and had some colour loss associated with weathering.

Aluminium was detected on all new CPGs and therefore was part of their matrix, but the higher concentrations were generally detected on soiled gloves. Aluminium concentrations decreased in both types of NBR gloves after use, which suggests that it was leached out, possibly due to the washing techniques. In the immersion experiments, there was a general reduction in the aluminium concentrations on the samples that were treated with the more viscous formulations, indicating a masking effect. The PVC gloves became sticky after four months exposure to the weather and this was when aluminium concentrations began to rise. This stickiness allowed contaminants to attach and to be retained on the surface. This trend was not evident on the Sol-Vex™ gloves as they did not dissociate as did the PVC but became brittle, and particulates were not able to be captured in the same manner. One Sol-Vex™ sample was particularly dirty, at seven months exposure, and it had a correspondingly high reading of aluminium.

Silicon was detected on all of the new CPGs and typically presented a similar profile to aluminium. Silicon was highest on the PVC gloves from the DP and OR groups and is suggestive of soil contamination. It was also detected in high concentrations on the NR gloves from the OR group and the used PVC/NBR gloves. There was a loss of silicon from the washing-up gloves after use, most likely due to cleaning. Silicon was

also a component of the OP formulations, as it was detected on the treated samples in the immersion experiments

Chlorine was a component of all the CPGs, although there was very little detected on the Hy-Care™ gloves. The relatively large chlorine peak on the unidentified gloves allowed the conclusion to be drawn that they were a type of thin PVC. Nearly all the gloves from the exchange program had less chlorine on them compared to their new counterparts. In some of the immersion experiments (Jetdip®) there were increased concentrations in the treated samples, which is possibly related to chemical reactions and migration. However, the general trend was for the formulations to occlude chlorine from the detector. Long-term exposure to the outdoors had little effect upon chlorine concentrations on PVC and NBR gloves.

Phosphorus and sulfur gave less significant peaks on some of the CPGs, which were found after use and in the laboratory experiments. These peaks were used as indicators for OP exposures.

Phosphorus was not detected on the new red PVC gloves. The highest concentrations of phosphorus were detected in the DP group. The gloves from this group were from sheep grazing properties where they had been worn for the application of a diazinon based sheep-dipping/jetting and showering formulation. This demonstrates the differing exposure risks that occur with the different tasks. Handling sheep that have been treated, such as pushing them into or out of the shower, dip or jetting apparatus and helping those in trouble, naturally exposes the farmers to greater risks of contamination from splashing. There were also relatively high levels of phosphorus on the PVC gloves from the OR group, again indicative of OP contamination. Phosphorus was detected in greater levels in the immersion experiments from those gloves treated with concentrated OP formulations. One minute's immersion was insufficient time to retain phosphorus from OP formulations. Phosphorus was only found as a component in one type of new CPGs, the black PVC. These gloves had no significant differences in phosphorus levels between the new and used.

Phosphorus was detected on the used NBR gloves, although in very small quantities, undoubtedly related to their cleaning procedures. This was supported by the Hy-Care™ results, where the unwashed gloves from the OR group had much higher levels of phosphorus than the ones from the TF group that had been washed. Phosphorus was also detected on the washing-up gloves from the BG group, which had not been used with OPs, but possibly this contamination was related to fertiliser usage.

Top Clip Blue Shield® is able to reside on PVC gloves even after application and seven months exposure to the outdoors. Phosphorus was not detected on the Sol-Vex™ gloves in the long-term exposure experiments. This demonstrated the inferior chemical resistance properties of PVC. It was demonstrated that phosphorus can act as a reasonably reliable indicator for OP exposure in PVC gloves but not Sol-Vex™.

Sulfur was a component of new red and black PVC gloves, both types of NBR gloves, the Hy-Care™ gloves and the Solvgard™ gloves. However, the general trend was for sulfur to be lost with use. The washing of gloves also decreased the concentration of sulfur. Long-term exposure to the outdoors and Top Clip Blue Shield® on PVC gloves gave variable results. As sulfur was also detected on the untreated gloves, it is apparent that it may have come from environmental sources. Sulfur concentrations were not affected by the same exposures on Sol-Vex™ gloves. Because of these factors sulfur can only be used as an indicator for OP exposure in controlled laboratory conditions.

The pesticide related peaks detected by GC-MS from the rinsates from the interior of some of the used PVC gloves included: tetramisole; a sheep/cattle drench, Nilverm®; a thermal artefact associated with the decomposition of carbaryl in the GC column; and paclobutrazol, a growth inhibitor found in Cultar® and Clipper®. Of course it is impossible to deduce how these pesticides came to reside in the glove linings. Possibilities include permeation, penetration, cross contamination and spilling the formulation inside the gloves. The linings can therefore act as reservoirs for pesticides and therefore increase the risk of exposure to the wearer. Wearing gloves occludes the skin, increases skin temperature, promotes vasodilatation and increases humidity. All these factors will enhance pesticide permeation through the skin.

8.5 Role Of Contaminants

Contaminants were also counted and some were analysed. Although contaminants cannot be technically classified as defects, they can abrade the polymer thus giving rise to failure and/or, depending on their constituents, react with the polymer and give rise to degradation. Contaminants certainly increased with glove use, as expected. New PVC gloves are tacky and therefore allow relatively easy adherence of contaminants. In the short-term exposure experiments, more contaminants were detected on the treated samples. This suggests that some form of cleaning procedure is desirable. Contaminants are an important observation of this research as their presence may have masked other defects.

8.6 Recommendations

There are seven recommendations for the future that have evolved from this research as follows.

8.6.1 Recommendation one

Polyvinyl chloride gloves made in China are of inferior quality, containing many inclusions and imperfections. The straight hand form of these types of gloves needs to be improved. The mould used for dipping should be contoured to provide a better fit. This would improve comfort, grasp and grip functions and would reduce the interstitial stresses that lead to failure. It would be preferable to have PVC gloves unlined with cotton knit fabric. This may make the glove less robust and it may be necessary to make the polymer thicker. If farmers prefer to wear lined gloves, there needs to be more research and development into a lining that does not act as a chemical reservoir. It would be preferable if such a lining could mask the residual odour caused by wearing PVC gloves. The area of CPG design requires much more research and development. The better option is for an Australian company to produce superior quality CPGs.

8.6.2 Recommendation two

Protocols and guidelines relating to CPG use need to be developed based on informed research from the agricultural safety sector. This information needs to be disseminated through various farming organisations, such as the National Farmers Federation and the Tasmanian Farmers and Graziers Association, to the pesticide manufacturers and to the rural retailers. A labelling system should be introduced to identify that some gloves are not suitable to be used for pesticide application. This has been recommended by other researchers, but this has not been taken up by manufacturers (Airey 1990; Bromwich *et al.* 1994-1995, p.4). A labelling system should be incorporated into the relevant glove standards.

8.6.3 Recommendation three

Sol-Vex™ gloves have superior chemical resistance properties compared with PVC gloves, but they are inadequate for outdoor use due to weathering. This means that they would require very frequent replacement and this would add considerably to farmers' operating costs, and it is unlikely that this procedure would be followed. It is recommended that farmers use PVC gloves and do not use them for more than one pesticide application season. Farmers should be encouraged to keep a record of the age and condition of their gloves and this could act as a reminder to purchase replacements.

8.6.4 Recommendation four

Very little is known about the affects of storage and cleaning on the properties of CPGs. Unfortunately the data from this research was confounded and no conclusions could be drawn. It was apparent that farmers treat their gloves haphazardly. More research is urgently needed to determine what type of cleaning procedures and storage are best suited for CPGs used in agricultural work. Recommendations should then be included on a label attached to CPGs.

8.6.5 Recommendation five

The double gloving technique used at TF should be followed up. The retention rates of Top Clip Blue Shield® on PVC gloves indicate that this method should be trialed with sheep farmers. It may be better to use unlined PVC gloves over NBR gloves.

8.6.6 Recommendation six

Polyvinyl chloride gloves should not be used for the application of Lorsban®, because the chemical rapidly permeates the gloves. Lorsban® was also very aggressive on Sol-Vex™ gloves exposed to sunlight for four hours. Neither of these gloves is suitable for use with this OP and research involving other polymers or copolymers is urgently required.

8.6.7 Recommendation seven

A limitation of the taxonomy approach used in this research was that the defect area could not be measured and therefore the results were semi-quantitative. The taxonomy method could be further refined by using a sophisticated image analysis technique so that the area of the defects could be measured automatically.

8.7 Conclusion

Several new domains for testing the efficacies of CPGs, as used in the agricultural sector, have been iniated. These methods are complementary to existing testing procedures. To diminish the risk of exposure to pesticides via farmers' hands, CPG design and materials requires improvement. Farmers need more knowledge about the various types of CPGs available, and their particular maintenance needs. I conclude that the popular CPGs in current use do not provide adequate protection for farmers health and safety.

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Appendix

Questionnaire: The New For Old Glove Exchange Program

University of
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Telephone [002] 202463

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GPO Box 252C, Hobart Tasmania
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Free Replacement Gloves

- Bring in your old gloves,
- Answer 4 questions
- and put in the box with your used gloves
- Select a new pair and then go to the service counter

I am conducting a study of the quality of chemically protective gloves used by farmers. I am looking at them microscopically to determine how they age and stand up to the rigours of farm life.

1) How long have you had the gloves? tick on dotted line

Less than 6 months.....

Less than 1 year.....

Less than 2 years.....

Over 2 years.....

2) Are they washed after each use? tick yes.....

no.....

a) with water yes.....

no.....

b) with water and detergent yes.....

no.....

PTO

3) Where do you store them ?

a) in the dark yes....

no.....

b) or in the light? yes....

no....

4) When you wear your gloves what chemicals are you using?

Comments welcome and thanks for your cooperation.